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(54) Title: TERNARY PHOTOINITIATOR SYSTEM FOR CURING OF EPOXY RESINS		
(57) Abstract Photocurable, addition polymerizable compositions contain an epoxy resin and a photoinitiator system containing (a) an epoxy resin and (b) a photoinitiator system comprising: (i) an iodonium salt; (ii) a visible light sensitizer; and (iii) an electron donor compound, wherein the photoinitiator system has a photoinduced potential of at least about 0mV relative to a standard solution of 2.9X10 ⁻⁵ moles/g diphenyl iodonium hexafluoroantimonate and 1.5X10 ⁻⁵ moles/g camphorquinone in 2-butanone. The compositions cure on exposure to light in the visible spectrum and are useful in a variety of applications, including dental adhesives and composites.		

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Ternary Photoinitiator System for Curing of Epoxy Resins

Field of the Invention

The invention relates to photocurable, addition polymerizable compositions that contain a ternary photoinitiator system that is activated on exposure to actinic radiation in the visible spectrum and methods of curing addition polymerizable compositions using the photoinitiator system. The invention is additionally directed to methods of curing addition polymerizable compositions using the ternary photoinitiator system.

Background of the Invention

Epoxy containing compounds are known to be curable using various cationic initiator systems. Smith, in U.S. Patent No. 4,256,828, describes photopolymerizable compositions that contain epoxides, an organic compound with hydroxyl functionality, and a photosensitive aromatic sulfonium or iodonium salt of a halogen containing complex ion. Hayase et al., U.S. Patent No. 4,835,193, describes photopolymerizable epoxy resin compositions that comprise an epoxy resin and a heteropoly-acid aromatic sulfonium salt as the photocuring catalyst. In WO 95/14716 Neckers et al. describe photohardenable compositions that comprise a cationically polymerizable compound, a xanthene or fluorone dye, a hydrogen donor, and an onium salt. Palazzotto et al., U.S. Patent No. 5,545,676, describes addition polymerization of free-radically polymerizable materials. The photoinitiator system described in that patent comprises an aryliodonium salt, a sensitizer, and an electron donor having an oxidation potential less than or equal to that of p-dimethoxybenzene.

PCT published application No. WO 96/13538 describes a system for curing epoxy compounds by exposure to visible light by use of a system comprising an aryliodonium salt and a sensitizer. Comparative Example 34 of this disclosure describes the use of one of the initiator systems of Palazzotto et al., U.S. Patent No. 5,545,676 in an epoxy/polyol resin system. N, N-dimethylbenzylamine

is used as the electron donor. The results of this experiment indicated that the use of this amine donor tended to retard the cure of the resin system.

Suppliers of cationically cured resins expressly warn against using organic amines in photoinitiated epoxy resins. An example of such a warning is found in Union Carbide literature regarding Cyracure® cycloaliphatic epoxides.

Summary of the Invention

We have discovered, and the invention provides, a photopolymerizable composition that contains an epoxy resin and a photoinitiator system containing an iodonium salt, a visible light sensitizer, and an electron donor compound, wherein the photoinitiator system has a photoinduced potential greater than or equal to that of 3-dimethylamino benzoic acid in a standard solution of 2.9×10^{-5} moles/g diphenyl iodonium hexafluoroantimonate and 1.5×10^{-5} moles/g camphorquinone in 2-butanone. Generally, 3-dimethylamino benzoic acid in this standard exhibits a photoinduced potential of at least about 115mV relative to a standard solution of 2.9×10^{-5} moles/g diphenyl iodonium hexafluoroantimonate and 1.5×10^{-5} moles/g camphorquinone in 2-butanone.

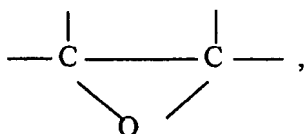
These compositions are curable on exposure to light having a wavelength of about 400 to 1000 nm, and the invention provides a method of addition photopolymerization comprising the step of irradiating a photopolymerizable composition with light having a wavelength of about 400 to 1000 nm until the composition gels or hardens, the composition comprising an epoxy resin and a photoinitiator system containing an iodonium salt, a visible light sensitizer, and an electron donor compound wherein the photoinitiator system has a photoinduced potential of at least about 100mV relative to a standard solution of 2.9×10^{-5} moles/g diphenyl iodonium hexafluoroantimonate and 1.5×10^{-5} moles/g camphorquinone in 2-butanone or has a photoinduced potential greater than or equal to that of 3-dimethylamino benzoic acid in a standard solution of 2.9×10^{-5} moles/g diphenyl iodonium hexafluoroantimonate and 1.5×10^{-5} moles/g camphorquinone in 2-butanone.

The initiator systems of the invention allow efficient cationic polymerization under conditions of room temperature and standard pressure. In addition, the initiator systems can, under appropriate conditions, initiate both cationic and free-radical polymerization. This property permits their use with a variety of photopolymerizable compositions. The use of these initiator systems actually results in the ability to cure epoxy systems otherwise not readily curable at room temperature with sensitizers and iodonium salts.

Detailed Description of the Invention

The photopolymerizable compositions of the invention are sensitive throughout the visible spectral region and photocure without appreciable application of heat. The term "visible light" is used throughout this application to refer to light having a wavelength of about 400 to 1000 nanometers (nm). Photopolymerization of the compositions takes place on exposure of the compositions to a source of actinic radiation having a wavelength within this spectral region.

The cationically polymerizable epoxy resins useful in the compositions of the invention are organic compounds having an oxirane ring, i.e., a group of the formula



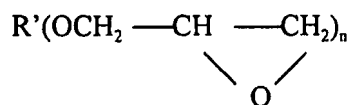
which is polymerizable by ring opening. Such materials, broadly called epoxides, include monomeric epoxy compounds and epoxides of the polymeric type and can be aliphatic, cycloaliphatic, aromatic or heterocyclic. These materials generally have, on the average, at least 1 polymerizable epoxy group per molecule, preferably at least about 1.5 and more preferably at least about 2 polymerizable epoxy groups per molecule. The polymeric epoxides include linear polymers having terminal epoxy groups (e.g., a diglycidyl ether of a polyoxyalkylene glycol), polymers having skeletal oxirane units (e.g., polybutadiene polyepoxide),

and polymers having pendent epoxy groups (e.g., a glycidyl methacrylate polymer or copolymer). The epoxides may be pure compounds or may be mixtures of compounds containing one, two, or more epoxy groups per molecule. The "average" number of epoxy groups per molecule is determined by dividing the total number of epoxy groups in the epoxy-containing material by the total number of epoxy-containing molecules present.

These epoxy-containing materials may vary from low molecular weight monomeric materials to high molecular weight polymers and may vary greatly in the nature of their backbone and substituent groups. For example, the backbone may be of any type and substituent groups thereon can be any group that does not substantially interfere with cationic cure at room temperature. Illustrative of permissible substituent groups include halogens, ester groups, ethers, sulfonate groups, siloxane groups, nitro groups, phosphate groups, and the like. The molecular weight of the epoxy-containing materials may vary from about 58 to about 100,000 or more.

Useful epoxy-containing materials include those which contain cyclohexene oxide groups such as epoxycyclohexanecarboxylates, typified by 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate, 3,4-epoxy-2-methylcyclohexylmethyl-3,4-epoxy-2-methylcyclohexane carboxylate, and bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate. For a more detailed list of useful epoxides of this nature, reference is made to the U.S. Patent No. 3,117,099, which is incorporated herein by reference.

Further epoxy-containing materials which are useful in the compositions of this invention include glycidyl ether monomers of the formula



where R' is alkyl or aryl and n is an integer of 1 to 6. Examples are glycidyl ethers of polyhydric phenols obtained by reacting a polyhydric phenol with an excess of chlorohydrin such as epichlorohydrin (e.g., the diglycidyl ether of 2,2-bis-(2,3-

epoxypropoxyphenol)-propane). Further examples of epoxides of this type are described in U.S. Patent No. 3,018,262, which is incorporated herein by reference, and in "Handbook of Epoxy Resins" by Lee and Neville, McGraw-Hill Book Co., New York (1967).

5 There are a host of commercially available epoxy resins which can be used in this invention. In particular, epoxides which are readily available include octadecylene oxide, epichlorohydrin, styrene oxide, vinyl cyclohexene oxide, glycidol, glycidylmethacrylate, diglycidyl ether of Bisphenol A (e.g., those available under the trade designations "Epon 828", "Epon 825", "Epon 1004" and
10 "Epon 1010" from Shell Chemical Co., "DER-331", "DER-332", and "DER-334", from Dow Chemical Co.), vinylcyclohexene dioxide (e.g., "ERL-4206" from Union Carbide Corp.), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexene carboxylate (e.g., "ERL-4221" or "CYRACURE UVR 6110" or UVR 6105" from Union Carbide Corp.), 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methyl-
15 cyclohexene carboxylate (e.g., "ERL-4201" from Union Carbide Corp.), bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate (e.g., "ERL-4289" from Union Carbide Corp.), bis(2,3-epoxycyclopentyl) ether (e.g., "ERL-0400" from Union Carbide Corp.), aliphatic epoxy modified from polypropylene glycol (e.g., "ERL-4050" and "ERL-4052" from Union Carbide Corp.), dipentene dioxide (e.g., "ERL-4269"
20 from Union Carbide Corp.), epoxidized polybutadiene (e.g., "Oxiron 2001" from FMC Corp.), silicone resin containing epoxy functionality, flame retardant epoxy resins (e.g., "DER-580", a brominated bisphenol type epoxy resin available from Dow Chemical Co.), 1,4-butanediol diglycidyl ether of phenolformaldehyde novolak (e.g., "DEN-431" and "DEN-438" from Dow Chemical Co.), and
25 resorcinol diglycidyl ether (e.g., "Kopoxite" from Koppers Company, Inc.), bis(3,4-epoxycyclohexyl)adipate (e.g., "ERL-4299" or "UVR-6128", from Union Carbide Corp.), 2-(3,4-epoxycyclohexyl-5, 5-spiro-3,4-epoxy) cyclohexane-meta-dioxane (e.g., "ERL-4234" from Union Carbide Corp.), vinylcyclohexene monoxide 1,2-epoxyhexadecane (e.g., "UVR-6216" from Union Carbide Corp.),
30 alkyl glycidyl ethers such as alkyl C₈-C₁₀ glycidyl ether (e.g., "HELOXY Modifier 7" from Shell Chemical Co.), alkyl C₁₂-C₁₄ glycidyl ether (e.g., "HELOXY

Modifier 8" from Shell Chemical Co.), butyl glycidyl ether (e.g., "HELOXY
Modifier 61" from Shell Chemical Co.), cresyl glycidyl ether (e.g., "HELOXY
Modifier 62" from Shell Chemical Co.), p-ter butylphenyl glycidyl ether (e.g.,
"HELOXY Modifier 65" from Shell Chemical Co.), polyfunctional glycidyl ethers
5 such as diglycidyl ether of 1,4-butanediol (e.g., "HELOXY Modifier 67" from
Shell Chemical Co.), diglycidyl ether of neopentyl glycol (e.g., "HELOXY
Modifier 68" from Shell Chemical Co.), diglycidyl ether of
cyclohexanedimethanol (e.g., "HELOXY Modifier 107" from Shell Chemical Co.),
trimethylol ethane triglycidyl ether (e.g., "HELOXY Modifier 44" from Shell
10 Chemical Co.), trimethylol propane triglycidyl ether (e.g., "HELOXY Modifier
48" from Shell Chemical Co.), polyglycidyl ether of an aliphatic polyol (e.g.,
"HELOXY Modifier 84" from Shell Chemical Co.), polyglycol diepoxide (e.g.,
"HELOXY Modifier 32" from Shell Chemical Co.), bisphenol F epoxides (e.g.,
"EPN-1138" or "GY-281" from Ciba-Geigy Corp.), 9,9-bis[4-(2,3-epoxypropoxy)-
15 phenyl]fluorenone (e.g., "Epon 1079" from Shell Chemical Co.).

Still other epoxy resins contain copolymers of acrylic acid esters or
glycidol such as glycidylacrylate and glycidylmethacrylate with one or more
copolymerizable vinyl compounds. Examples of such copolymers are 1:1 styrene-
glycidylmethacrylate, 1:1 methylmethacrylate-glycidylacrylate and a 62.5:24:13.5
20 methylmethacrylate-ethyl acrylate-glycidylmethacrylate.

Other useful epoxy resins are well known and contain such epoxides
as epichlorohydrins, alkylene oxides, e.g., propylene oxide, styrene oxide; alkenyl
oxides, e.g., butadiene oxide; glycidyl esters, e.g., ethyl glycidate.

The polymers of the epoxy resin may optionally contain other
25 functionalities that do not substantially interfere with cationic cure at room
temperature.

Blends of various epoxy-containing materials are also contemplated
in this invention. Examples of such blends include two or more weight average
molecular weight distributions of epoxy-containing compounds, such as low
30 molecular weight (below 200), intermediate molecular weight (about 200 to
10,000) and higher molecular weight (above about 10,000). Alternatively or

additionally, the epoxy resin may contain a blend of epoxy-containing materials having different chemical natures, such as aliphatic and aromatic, or functionalities, such as polar and non-polar. Other cationically polymerizable polymers may additionally be incorporated, if desired.

5 If desired, the composition can also contain a free-radically polymerizable material, including ethylenically unsaturated monomer, monomers or oligomers or polymers. Suitable materials contain at least one ethylenically unsaturated bond, and are capable of undergoing addition polymerization. Such free radically polymerizable materials include mono-, di- or poly- acrylates and
10 methacrylates such as methyl acrylate, methyl methacrylate, ethyl acrylate, isopropyl methacrylate, n-hexyl acrylate, stearyl acrylate, allyl acrylate, glycerol diacrylate, glycerol triacrylate, ethyleneglycol diacrylate, diethyleneglycol diacrylate, triethyleneglycol dimethacrylate, 1,3-propanediol diacrylate, 1,3-propanediol dimethacrylate, trimethylolpropane triacrylate, 1,2,4-butanetriol
15 trimethacrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, sorbitol hexacrylate, bis[1-(2-acryloxy)]-p-ethoxyphenyldimethylmethane, bis[1-(3-acryloxy-2-hydroxy)]-p-propoxyphenyldimethylmethane, and trishydroxyethyl-isocyanurate trimethacrylate; the bis-acrylates and bis-methacrylates of polyethylene glycols of
20 molecular weight 200-500, copolymerizable mixtures of acrylated monomers such as those in U.S. Pat. No. 4,652,274, and acrylated oligomers such as those of U.S. Pat. No. 4,642,126; and vinyl compounds such as styrene, diallyl phthalate, divinyl succinate, divinyl adipate and divinylphthalate. Mixtures of two or more of these free radically polymerizable materials can be used if desired.

25 If desired, the polymerizable material(s) may contain both epoxy and free-radically polymerizable functionalities in a single molecule. These may be obtained by reacting a di- or poly-epoxide with one or more equivalents of an ethylenically unsaturated carboxylic acid. Examples of such materials include the reaction product of UVR-6105 (available from Union Carbide) or DER 332 with
30 one equivalent of methacrylic acid. Commercially available materials having

epoxy and free-radically polymerizable functionalities include the "Cyclomer" series, such as Cyclomer M100 or M101, available from Daicel Chemical, Japan.

The epoxy resin and optional free radically polymerizable material(s) are combined with a three component or ternary photoinitiator system.

5 Three component initiator systems are described in Palazzotto et al., U.S. Patent No. 5,545,676, which is incorporated herein by reference. The first component in the photoinitiator system is an iodonium salt, i.e., a diaryliodonium salt. The iodonium salt should be soluble in the monomer and preferably is shelf-stable, meaning it does not spontaneously promote polymerization when dissolved therein
10 in the presence of the sensitizer and donor. Accordingly, selection of a particular iodonium salt may depend to some extent upon the particular monomer, sensitizer and donor chosen. Suitable iodonium salts are described in U.S. Pat. Nos. 3,729,313, 3,741,769, 3,808,006, 4,250,053 and 4,394,403, the iodonium salt disclosures of which are incorporated herein by reference. The iodonium salt can
15 be a simple salt, containing an anion such as Cl^- , Br^- , I^- or $\text{C}_4\text{H}_9\text{SO}_3^-$; or a metal complex salt containing an antimonate, arsenate, phosphate or borate such as SbF_6^- , OH^- or AsF_6^- . Mixtures of iodonium salts can be used if desired.

Examples of useful aromatic iodonium complex salt photoinitiators include: diphenyliodonium tetrafluoroborate; di(4-methylphenyl)iodonium
20 tetrafluoroborate; phenyl-4-methylphenyliodonium tetrafluoroborate; di(4-heptylphenyl)iodonium tetrafluoroborate; di(3-nitrophenyl)iodonium hexafluorophosphate; di(4-chlorophenyl)iodonium hexafluorophosphate; di(naphthyl)iodonium tetrafluoroborate; di(4-trifluoromethylphenyl)iodonium tetrafluoroborate; diphenyliodonium hexafluorophosphate; di(4-
25 methylphenyl)iodonium hexafluorophosphate; diphenyliodonium hexafluoroarsenate; di(4-phenoxyphenyl)iodonium tetrafluoroborate; phenyl-2-thienyliodonium hexafluorophosphate; 3,5-dimethylpyrazolyl-4-phenyliodonium hexafluorophosphate; diphenyliodonium hexafluoroantimonate; 2,2'-diphenyliodonium tetrafluoroborate; di(2,4-dichlorophenyl)iodonium
30 hexafluorophosphate; di(4-bromophenyl)iodonium hexafluorophosphate; di(4-methoxyphenyl)iodonium hexafluorophosphate; di(3-carboxyphenyl)iodonium

hexafluorophosphate; di(3-methoxycarbonylphenyl)iodonium
hexafluorophosphate; di(3-methoxysulfonylphenyl)iodonium hexafluorophosphate;
di(4-acetamidophenyl)iodonium hexafluorophosphate; di(2-benzothieryl)iodonium
hexafluorophosphate; and diphenyliodonium hexafluoroantimonate.

5 Of the aromatic iodonium complex salts which are suitable for use
in the compositions of the invention diaryliodonium hexafluorophosphate and
diaryliodonium hexafluoroantimonate are among the preferred salts. These salts
are preferred because, in general, they promote faster reaction, and are more
soluble in inert organic solvents than are other aromatic iodonium salts of complex
10 ions.

 The aromatic iodonium complex salts may be prepared by
metathesis of corresponding aromatic iodonium simple salts (such as, for example,
diphenyliodonium bisulfate) in accordance with the teachings of Beringer et al., J.
Am. Chem. Soc. 81,342 (1959). Thus, for example, the complex salt
15 diphenyliodonium tetrafluoroborate is prepared by the addition at 60°C of an
aqueous solution containing 29.2 g silver fluoroborate, 2 g fluoroboric acid, and
0.5 g phosphorous acid in about 30 ml of water to a solution of 44 g (139
millimoles) of diphenyliodonium chloride. The silver halide that precipitates is
filtered off and the filtrate concentrated to yield diphenyliodonium fluoroborate
20 which may be purified by recrystallization.

 The aromatic iodonium simple salts may be prepared in accordance
with Beringer et al., above, by various methods including (1) coupling of two
aromatic compounds with iodyl sulfate in sulfuric acid, (2) coupling of two
aromatic compounds with an iodate in acetic acid-acetic anhydride-sulfuric acid,
25 (3) coupling of two aromatic compounds with an iodine acrylate in the presence of
an acid, and (4) condensation of an iodoso compound, an iodoso diacetate, or an
iodoxy compound with another aromatic compound in the presence of an acid.
Diphenyliodonium bisulfate is prepared by method (3), for example, by the
addition over a period of eight hours at below 5°C of a mixture of 35 ml of conc.
30 sulfuric acid and 50 ml of acetic anhydride to a well-stirred mixture of 55.5 ml of
benzene, 50 ml of acetic anhydride, and 53.5g of potassium iodate. The mixture is

stirred for an additional four hours at 0°-5°C and at room temperature (about 25°C) for 48 hours and treated with 300 ml of diethyl ether. On concentration, crude diphenyliodonium bisulfate precipitates and may be purified by recrystallization if desired.

5 The second component in the photoinitiator system is the sensitizer. The sensitizer should be soluble in the photopolymerizable composition, free of functionalities that would substantially interfere with the cationic curing process, and capable of light absorption somewhere within the range of wavelengths between about 300 and about 1000 nanometers.

10 Suitable sensitizers are believed to include compounds in the following categories: ketones, coumarin dyes (e.g., ketocoumarins), xanthene dyes, acridine dyes, thiazole dyes, thiazine dyes, oxazine dyes, azine dyes, aminoketone dyes, porphyrins, aromatic polycyclic hydrocarbons, p-substituted aminostyryl ketone compounds, aminotriaryl methanes, merocyanines, squarylium
15 dyes and pyridinium dyes. Ketones (e.g., monoketones or alpha-diketones), ketocoumarins, aminoarylketones and p-substituted aminostyryl ketone compounds are preferred sensitizers. For applications requiring deep cure (e.g., cure of highly-filled composites), it is preferred to employ sensitizers having an extinction
20 coefficient below about 1000 l·mole⁻¹·cm⁻¹, more preferably about or below 100 l·mole⁻¹·cm⁻¹, at the desired wavelength of irradiation for photopolymerization. The alpha-diketones are an example of a class of sensitizers having this property, and are particularly preferred for dental applications

By way of example, a preferred class of ketone sensitizers has the formula:

25



where X is CO or CR¹R² where R¹ and R² can be the same different, and can be hydrogen, alkyl, alkaryl or aralkyl, b is zero, and A and B can be the same or
30 different and can be substituted (having one or more non-interfering substituents) or unsubstituted aryl, alkyl, alkaryl, or aralkyl groups, or together A and B can

form a cyclic structure which can be a substituted or unsubstituted cycloaliphatic, aromatic, heteroaromatic or fused aromatic ring.

Suitable ketones of the above formula include monoketones ($b=0$) such as 2,2-, 4,4- or 2,4-dihydroxybenzophenone, di-2-pyridyl ketone, di-2-furanyl ketone, di-2-thiophenyl ketone, benzoin, fluorenone, chalcone, Michler's ketone, 2-fluoro-9-fluorenone, 2-chlorothioxanthone, acetophenone, benzophenone, 1- or 2-acetonaphthone, 9-acetylanthracene, 2-, 3- or 9-acetylphenanthrene, 4-acetylbiphenyl, propiophenone, n-butyrophenone, valerophenone, 2-, 3- or 4-acetylpyridine, 3-acetylcoumarin and the like. Suitable diketones include aralkyldiketones such as anthraquinone, phenanthrenequinone, o-, m- and p-diacetylbenzene, 1,3-, 1,4-, 1,5-, 1,6-, 1,7- and 1,8-diacetylnaphthalene, 1,5-, 1,8- and 9,10-diacetylanthracene, and the like. Suitable I-diketones ($b=1$ and $x=CO$) include 2,3-butanedione, 2,3-pentanedione, 2,3-hexanedione, 3,4-hexanedione, 2,3-heptanedione, 3,4-heptanedione, 2,3-octanedione, 4,5-octanedione, benzil, 2,2'-3,3'- and 4,4'-dihydroxybenzil, furil, di-3,3'-indolyethanedione, 2,3-bornanedione (camphorquinone), biacetyl, 1,2-cyclohexanedione, 1,2-naphthaquinone, acenaphthaquinone, and the like.

Examples of particularly preferred visible light sensitizers include camphorquinone; glyoxal; biacetyl; 3,3,6,6-tetramethylcyclohexanedione; 3,3,7,7-tetramethyl-1,2-cycloheptanedione; 3,3,8,8-tetramethyl-1,2-cyclooctanedione; 3,3,18,18-tetramethyl-1,2-cyclooctadecanedione; dipivaloyl; benzil; furil; hydroxybenzil; 2,3-butanedione; 2,3-pentanedione; 2,3-hexanedione; 3,4-hexanedione; 2,3-heptanedione; 3,4-heptanedione; 2,3-octanedione; 4,5-octanedione; and 1,2-cyclohexanedione. Of these, camphorquinone is the most highly preferred sensitizer.

The third component of the initiator system is an electron donor. The electron donor compound(s) should meet one of the requirements set forth below and should be soluble in the polymerizable composition. The donor can also be selected in consideration of other factors, such as shelf stability and the nature of the polymerizable materials, iodonium salt and sensitizer chosen. A class of donor compounds that may be useful in the inventive systems may be selected from some

of the donors described in Palazzotto et al., U.S. Patent No. 5,545,676. Possible donor compounds that meet the criteria set forth by Palazzotto et al. must then be tested using one or both of the methods set forth below to determine if they will be useful donors for the photopolymerizable compositions of the invention.

5 The donor is typically an alkyl aromatic polyether or an alkyl, aryl amino compound wherein the aryl group is substituted by one or more electron withdrawing groups. Examples of suitable electron withdrawing groups include carboxylic acid, carboxylic acid ester, ketone, aldehyde, sulfonic acid, sulfonate and nitrile groups.

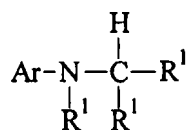
10 The suitability of a compound for usefulness in the compositions of the invention may be determined by measuring the photoinduced potential of a sample photoinitiator system that includes the compound. The photoinduced potential can be evaluated using one of two methods. In the first, a standard solution is prepared that contains 2.9×10^{-5} moles/g of diphenyl iodonium
15 hexafluoroantimonate and 1.5×10^{-5} moles/g of camphorquinone in 2-butanone. A pH electrode is then immersed in the solution and a pH meter is calibrated to zero mV. A test solution of the standard solution and the compound is prepared next using the compound at a concentration of 2.9×10^{-5} moles/g. This test solution is irradiated using blue light having a wavelength of about 400 to 500 nm having an
20 intensity of about 200 to 400 mW/cm² for about 5 to 10 seconds. Millivolts relative to the standard solution are then determined by immersing the pH electrode in the test solution and obtaining a mV reading on the pH meter. For this method, useful donors are those compounds that provide a reading of at least 100mV relative to the standard solution and provide a gel time for the compositions that
25 fail to gel at 25 C in the absence of donor. Higher mV readings are generally indicative of greater activity, and to obtain a more rapid cure reading of at least about 100mV are preferred.

 In some instances there may be some uncertainty regarding the outcome of the above procedure. This may be due to questions or uncertainty
30 arising from the instrumentation employed, from the way the procedure was carried out, or other factors, or one may wish to verify the suitability of a particular

compound. A second test may be performed to verify the result obtained by following the above procedure and resolve any such uncertainty.

The second method involves the evaluation of the photoinduced potential of an initiator system that includes the compound compared to a system that includes 3-dimethylamino benzoic acid. For this method, a standard solution of 2.9×10^{-5} moles/g diphenyl iodonium hexafluoroantimonate, 1.5×10^{-5} moles/g camphorquinone and 2.9×10^{-5} moles/g of 3-dimethylamino benzoic acid in 2-butanone is prepared. A pH electrode is then immersed in the solution and a pH meter is calibrated to zero mV. The standard solution is irradiated with blue light having a wavelength of between about 400-500 nm and an intensity of about 200 to 400 mW/cm² for about 5 to 10 seconds using a focused light source such as a dental curing light. After light exposure, the potential of the solution is measured by immersing a pH electrode in the irradiated standard solution and reading the potential in mV using a pH meter. A test solution is then prepared using 2.9×10^{-5} moles/g of diphenyl iodonium hexafluoroantimonate, 1.5×10^{-5} moles/g of camphorquinone and 2.9×10^{-5} moles/g of the compound in 2-butanone. The test solution is irradiated and the photoinduced potential measured using the same technique as described for the standard solution. If the test solution has a photoinduced potential that is the same as or greater than that of the 3-dimethylamino benzoic acid containing standard solution, then the compound is a useful donor.

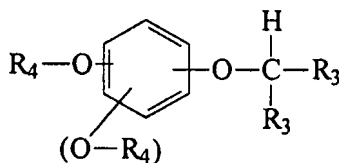
A preferred group of alkyl, aryl amine donor compounds is described by the following structural formula:



wherein R¹ are independently H, C₁₋₁₈ alkyl that is optionally substituted by one or more halogen, -CN, -OH, -SH, C₁₋₁₈ alkoxy, C₁₋₁₈ alkylthio, C₃₋₁₈ cycloalkyl, aryl, COOH, COOC₁₋₁₈ alkyl, (C₁₋₁₈ alkyl)₀₋₁-CO-C₁₋₁₈ alkyl, SO₃R², CN or or aryl that is optionally substituted by one or more electron withdrawing groups; and Ar is aryl that is substituted by one or more electron withdrawing groups. Suitable electron

withdrawing groups include $-\text{COOH}$, $-\text{COOR}^2$, $-\text{SO}_3\text{R}^2$, $-\text{CN}$, $-\text{CO}-\text{C}_{1-18}$ alkyl and $-\text{C}(\text{O})\text{H}$ groups.

A preferred group of aryl alkyl polyethers has the following structural formula:



5

wherein $n = 1-3$ each R_3 is independently H or C_{1-18} alkyl that is optionally substituted by one or more halogen, $-\text{CN}$, $-\text{OH}$, $-\text{SH}$, C_{1-18} alkoxy, C_{1-18} alkylthio, C_{3-18} cycloalkyl, aryl, substituted aryl, $-\text{COOH}$, $-\text{COOC}_{1-18}$ alkyl, $-(\text{C}_{1-18} \text{ alkyl})_{0-1}-\text{COH}$, $-(\text{C}_{1-18} \text{ alkyl})_{0-1}-\text{CO}-\text{C}_{1-18}$ alkyl, $-\text{CO}-\text{C}_{1-18}$ alkyl, $-\text{C}(\text{O})\text{H}$ or $-\text{C}_{2-18}$ alkenyl groups and each R_4 can be C_{1-18} alkyl that is optionally substituted by one or more halogen, $-\text{CN}$, $-\text{OH}$, $-\text{SH}$, C_{1-18} alkoxy, C_{1-18} alkylthio, C_{3-18} cycloalkyl, aryl, substituted aryl, $-\text{COOH}$, $-\text{COOC}_{1-18}$ alkyl, $-(\text{C}_{1-18} \text{ alkyl})_{0-1}-\text{COH}$, $-(\text{C}_{1-18} \text{ alkyl})_{0-1}-\text{CO}-\text{C}_{1-18}$ alkyl, $-\text{CO}-\text{C}_{1-18}$ alkyl, $-\text{C}(\text{O})\text{H}$ or $-\text{C}_{2-18}$ alkenyl groups.

In each of the above formulas the alkyl groups can be straight-chain or branched, and the cycloalkyl group preferably has 3 to 6 ring carbon atoms but may have additional alkyl substitution up to the specified number of carbon atoms. The aryl groups may be carbocyclic or heterocyclic aryl, but are preferably carbocyclic and more preferably phenyl rings.

Preferred donor compounds include 4-dimethylaminobenzoic acid, ethyl 4-dimethylaminobenzoate, 3-dimethylaminobenzoic acid, 4-dimethylaminobenzoin, 4-dimethylaminobenzaldehyde, 4-dimethylaminobenzonitrile and 1,2,4-trimethoxybenzene.

The photoinitiator compounds are provided in an amount effective to initiate or enhance the rate of cure of the resin system. It has been found that the amount of donor that is used can be critical particularly when the donor is an amine. Too much donor can be deleterious to cure properties. Preferably, the sensitizer is present in about 0.05-5.0 weight percent based on resin compounds of

the overall composition. More preferably, the sensitizer is present at 0.10-1.0 weight percent. Similarly, the iodonium initiator is preferably present at 0.05-10.0 weight percent, more preferably at 0.10-5.0 weight percent, and most preferably 0.50-3.0 weight percent. Likewise, the donor is preferably present at 0.01-5.0 weight percent, more preferably 0.05-1.0 weight percent, and most preferably 0.05-0.50 weight percent.

The photopolymerizable compositions of the invention are prepared by simply admixing, under "safe light" conditions, the components of the inventive compositions. Suitable inert solvents may be employed if desired when effecting this mixture. Any solvent may be used which does not react appreciably with the components of the inventive compositions. Examples of suitable solvents include acetone, dichloromethane, and acetonitrile. A liquid material to be polymerized may be used as a solvent for another liquid or solid material to be polymerized. Solventless compositions can be prepared by simply dissolving the aromatic iodonium complex salt and sensitizer in the epoxy resin polyol mixture with or without the use of mild heating to facilitate dissolution.

The compositions of the present invention provide a very useful combination of cure speed, cure depth and shelf life. They cure well even when loaded with large amounts of fillers, and can be used in a variety of applications including graphic arts imaging (e.g. for color proofing systems, curable inks, or silverless imaging), printing plates (e.g. projection plates or laser plates), photoresists, solder masks, electronic conformal coatings, coated abrasives, magnetic media, photocurable adhesives (e.g. for orthodontics) and photocurable composites (e.g., for autobody repair or dentistry).

The photopolymerizable compositions of the invention are prepared by simply admixing, under "safe light" conditions, the components of the inventive compositions. Suitable inert solvents may be employed if desired when effecting this mixture. Any solvent may be used which does not react appreciably with the components of the inventive compositions. Examples of suitable solvents include acetone, dichloromethane, and acetonitrile. A liquid material to be polymerized may be used as a solvent for another liquid or solid material to be polymerized.

Solventless compositions can be prepared by simply dissolving the aromatic iodonium complex salt and sensitizer in the epoxy resin with or without the use of mild heating to facilitate dissolution.

5 Dental applications particularly benefit from the unique compositions of the present invention. Until now, acrylate and methacrylate chemistry has been used extensively for adhesive and restorative dental compositions. This chemistry has the advantage of being curable with visible light using photoinitiator systems, but has the disadvantage of undergoing a relatively high degree of shrinkage during the polymerization process. In contrast, during
10 polymerization the epoxy resins found in the compositions of the present invention shrink significantly less than the acrylate and methacrylate resins of the prior art. The present invention provides a system for curing epoxy resins in an acceptable time frame and to a sufficient depth using visible light source equipment already available in the dental office.

15 The dental materials may be filled or unfilled and include dental materials such as direct esthetic restorative materials (e.g., anterior and posterior restoratives), prostheses, adhesives and primers for oral hard tissues, sealants, veneers, cavity liners, orthodontic bracket adhesives for use with any type of bracket (such as metal, plastic and ceramic), crown and bridge cements, artificial
20 crowns, artificial teeth, dentures, and the like. These dental materials are used in the mouth and are disposed adjacent to natural teeth. The phrase "disposed adjacent to" as used herein refers to the placing of a dental material in temporary or permanent bonding (e.g., adhesive) or touching (e.g., occlusal or proximal) contact with a natural tooth. The term "composite" as used herein refers to a filled dental
25 material. The term "restorative" as used herein refers to a composite which is polymerized after it is disposed adjacent to a tooth. The term "prosthesis" as used herein refers to a composite which is shaped and polymerized for its final use (e.g., as crown, bridge, veneer, inlay, onlay or the like) before it is disposed adjacent to a tooth. The term "sealant" as used herein refers to a lightly filled composite or to an
30 unfilled dental material which is cured after it is disposed adjacent to a tooth.

"Polymerizable" refers to curing or hardening the dental material, e.g., by free-radical, cationic or mixed reaction mechanisms.

5 In certain applications, the use of a filler may be appropriate. The choice of filler affects important properties of the composite such as its appearance, radiopacity and physical and mechanical properties. Appearance is affected in part by adjustment of the amounts and relative refractive indices of the ingredients of the composite, thereby allowing alteration of the translucence, opacity or pearlescence of the composite. Epoxy resin compositions of the invention, either alone or in admixture with diluent monomer, can be prepared with refractive
10 indices which approach or approximate the refractive indices of fillers such as quartz (refractive index 1.55), submicron silica (refractive index 1.46), and 5.5:1 mole ratio SiO:ZrO, non-vitreous microparticles (refractive index 1.54). In this way the appearance of the dental material can, if desired, be made to closely approximate the appearance of natural dentition.

15 Radiopacity is a measurement of the ability of the composite to be detected by x-ray examination. Frequently a radiopaque composite will be desirable, for instance, to enable the dentist to determine whether or not a dental restoration remains sound. Under other circumstances a non-radiopaque composite may be desirable.

20 The amount of filler which is incorporated into the composite, referred to herein as the "loading level" and expressed as a weight percent based on the total weight of the dental material, will vary depending on the type of filler, the epoxy resin and other components of the composition, and the end use of the composite.

25 For some dental materials, such as sealants, the epoxy resin compositions of the invention can be lightly filled (e.g., having a loading level of less than about 40 weight percent) or unfilled. Preferably the viscosity of the dental material is sufficiently low to allow its penetration into pits and fissures of occlusal tooth surfaces as well as into etched areas of enamel, thereby aiding in the
30 retention of the dental material. In applications where high strength or durability are desired (e.g., anterior or posterior restoratives, prostheses, crown and bridge

cements, artificial crowns, artificial teeth and dentures) the loading level can be as high as about 95 weight percent. For most dental restorative and prosthetic applications a loading level of between about 70 and 90 weight percent is generally preferred.

5 Fillers may be selected from one or more of any material suitable for incorporation in compositions used for medical applications, such as fillers currently used in dental restorative compositions and the like. The filler is finely divided and preferably has a maximum particle diameter of less than about 50 micrometers and an average particle diameter of less than about 10 micrometers.

10 The filler can have a unimodal or polymodal (e.g., bimodal) particle size distribution. The filler can be an inorganic material. It can also be a crosslinked organic material that is insoluble in the polymerizable resin, and is optionally filled with inorganic filler. The filler should in any event be non-toxic and suitable for use in the mouth. The filler can be radiopaque, radiolucent or nonradiopaque.

15 Examples of suitable inorganic fillers are naturally-occurring or synthetic materials such as quartz, nitrides (e.g., silicon nitride), glasses derived from, for example Ce, Sb, Sn, Zr, Sr, Ba and Al, colloidal silica, feldspar, borosilicate glass, kaolin, talc, titania, and zinc glass; low Mohs hardness fillers such as those described in U.S. Patent No. 4,695,251; and submicron silica

20 particles (e.g., pyrogenic silicas such as the "Aerosil" Series "OX 50", "130", "150" and "200" silicas sold by Degussa and "Cab-O-Sil M5" silica sold by Cabot Corp.). Examples of suitable organic filler particles include filled or unfilled pulverized polycarbonates, polyepoxides, and the like. Preferred filler particles are quartz, submicron silica, and non-vitreous microparticles of the type described in

25 U.S. Patent No. 4,503,169. Metallic fillers may also be incorporated, such as particulate metal filler made from a pure metal such as those of Groups IVA, VA, VIA, VIIA, VIII, IB, or IIB, aluminum, indium, and thallium of Group IIIB, and tin and lead of Group IVB, or alloys thereof. Conventional dental amalgam alloy powders, typically mixtures of silver, tin, copper, and zinc, may also optionally be

30 incorporated. The particulate metallic filler preferably has an average particle size of about 1 micron to about 100 microns, more preferably 1 micron to about 50

microns. Mixtures of these fillers are also contemplated, as well as combination fillers made from organic and inorganic materials. Fluoroaluminosilicate glass fillers, either untreated or silanol treated, are particularly preferred. These glass fillers have the added benefit of releasing fluoride at the site of dental work when placed in the oral environment.

Optionally, the surface of the filler particles may be treated with a surface treatment such as a coupling agent in order to enhance the bond between the filler and the polymerizable resin. The coupling agent may be functionalized with reactive curing groups, such as acrylates, methacrylates, epoxies, and the like. Examples of coupling agents include silanes such as gamma-methacryloxypropyltrimethoxysilane, gamma-mercaptopropyltriethoxysilane, beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, gamma-glycidoxypyltrimethoxysilane, and the like.

The materials of the present invention can also contain suitable adjuvants such as accelerators, inhibitors, absorbers, stabilizers, pigments, dyes, viscosity modifiers, surface tension depressants and wetting aids, antioxidants, and other ingredients well known to those skilled in the art.

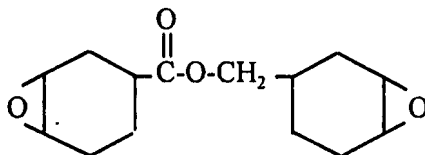
The amounts and types of each ingredient in the dental material should be adjusted to provide the desired physical and handling properties before and after cure. For example, the cure rate, cure stability, fluidity, compressive strength, tensile strength and durability of the dental material typically are adjusted in part by altering the types and amounts of polymerization initiator(s) and, if present, the loading and particle size distribution of filler(s). Such adjustments typically are carried out empirically based on experience with dental materials of the prior art.

When the dental material is applied to a tooth, the tooth can optionally be pre-treated with a primer such as dentin or enamel adhesive by methods known to those skilled in the art.

The invention is further described by reference to the following examples, which are understood to be merely illustrative and not limiting the invention in any way.

Example 1

A stock solution of an epoxy resin material was prepared by combining 0.50 g camphorquinone, 1.50 g diphenyliodoniumhexafluoroantimonate (DPI SbF₆) and 98.00 g UVR 6105 cycloaliphatic diepoxide, and stirring until homogeneous in the absence of light. UVR 6105 is a cycloaliphatic diepoxide having the following formula:



A stock solution of an epoxy resin/acrylate material was prepared by transferring 0.50 g camphorquinone and 1.50 g DPI SbF₆ to a glass jar followed by the addition of approximately 0.20 gram of dichloromethane solvent, 88.2 grams of UVR 6105 and 9.80 grams of Ebecryl 1830 polyester hexacrylate from Radcure Specialties. The mixture was stirred until homogeneous in the absence of light.

A variety of donor compounds were evaluated for their photoinduced potential. To evaluate the photoinduced potential of the compounds, a stock initiator solution was prepared by transferring 0.50 grams camphorquinone and 3.00 grams of DPI SbF₆ to a 250 ml polyethylene screw-top bottle. Two hundred grams of 99.5+% 2-butanone were transferred to the polyethylene bottle and the contents mixed until homogeneous. The resulting solution contained approximately 2.9×10^{-5} moles DPISbF₆/gram of stock initiator solution and 1.5×10^{-5} moles CPQ/gram of SL1. The electron donor additives were evaluated at a concentration of 2.9×10^{-5} moles donor/gram of SL1. Samples were prepared by transferring 1.16×10^{-4} moles of donor to a 13ml glass vial followed by the addition of 4.0 grams of the stock initiator solution. Vials were capped and vigorously shaken until homogeneous. Samples were then evaluated for relative potential according to the following procedure:

A semi-micro combination pH electrode (Corning model 476540) was connected to a pH meter with millivolt capability (Beckman Φ P/N 123133). The stock initiator solution was used as the millivolt standard in this evaluation. Four grams of the stock initiator solution were transferred to a 13 ml glass vial along with a micro-magnetic stir bar. The sample was placed above a magnetic stirrer which initiated slow stirring of the sample. The electrode was rinsed with water followed by ethanol and then thoroughly dried with a paper towel. The electrode was immersed in the stock initiator solution and the millivolt reading calibrated to read 0.00 mV. The electrode was removed and the sample was irradiated with a Visilux dental curing light having an intensity of about 200 mW/cm² at a wavelength of 400 to 500 nm for 10 seconds by placing the tip of the light guide directly flush with the center bottom of the vial. Following irradiation the sample was capped and mixed thoroughly by shaking for about 5 seconds. The electrode was rinsed, cleaned thoroughly with ethanol, blotted dry and immersed in the irradiated solution. The millivolts relative to the control was established by pressing the mV button on the pH meter until a stable reading was obtained. The above procedure was repeated with the various donor solutions. The electrode was calibrated with unirradiated stock initiator solution before each run as described previously.

The donor compounds were evaluated for their effect on cure speed of two stock resin solutions. Approximately one gram samples were prepared by transferring 2.9×10^{-5} moles of each prospective donor to 1 dram glass vials followed by 1 drop of dichloromethane solvent and 1.0 grams of the stock epoxy resin or epoxy resin/acrylate material. The ingredients were mixed until homogeneous. Each sample was examined for gel time by transferring the solution to a 6mm diameter and 2.5 mm thick Teflon mold with a polyester film clamped in direct contact with the bottom face. The sample was placed directly beneath the light guide of a Visilux 2 dental curing light at a distance of 10 mm for the epoxy samples or 30 mm for the epoxy/acrylate samples. Samples were irradiated up to a maximum of 120 seconds and probed to establish hard gel times. Results are

reported in Table 1. Throughout the examples, "NC" means that the material did not cure and "NT" means that the material was not tested.

Table 1

Sample Number	Donor Compound	gms donor/ gm resin	gel time epoxy (sec)	gel time epoxy/acrylate (sec)	mV (initial) MEK	mV (photo) MEK
1	none	none	NC	NC	0	-25
2	4-dimethylaminobenzoic acid	0.0047	14	12	-11	184
3	ethyl 4-dimethylaminobenzoate	0.0053	15	13	-12	200
4	3-dimethylaminobenzoic acid	0.0047	23	20	-5	115
6	1,2,4-trimethoxybenzene	0.0053	35	25	-3	233
7	4-dimethylaminobenzoin	0.0068	30	29	-13.4	261
8	N-phenylglycine	0.0044	45	35	-16.4	161
9	4-dimethylaminobenzonitrile	0.0045	60	60	9.7	266
10	4-dimethylaminobenzaldehyde	0.0043	75	60	8	245
11	4-dimethylaminophenethanol	0.0046	NC	3hrs	-83.2	17
12	dimethylaniline	0.0043	<12hrs	3hrs	-55	54
13	2,5-dimethoxybenzylalcohol	0.0049	<12hrs	3hrs	30.8	52
14	tetrahydrofurfural alcohol	0.0030	<12hrs	NC	-34	-10
15	1,2,3-trimethoxybenzene	0.0050	NC	3hrs	-1.9	5
16	1,3,5-trimethoxybenzene	0.0050	NC	3hrs	10.1	28
17	benzyl alcohol	0.0031	<12hrs	3hrs	-13.7	24
18	4-(dimethylamino) phenylacetic acid	0.0052	<12hrs	NT	-93.5	-15
19	ethyl 2-dimethylaminobenzoate	0.0047	<12hrs	NT	-78	19
20	pentamethylaniline	0.0050	NC	NT	10	71.3
21	N,N-dimethylbenzylamine	0.0040	NC	NC	-189.7	-170
22	triethanolamine	0.0042	NC	NC	-171	-162
23	dihydroxyethyl-p-toluidine	0.0058	NC	NC	-180	-98
24	N(2,4-dimethyl-phenyl)N,N(bis-2-hydroxyethylamine)	0.0059	NC	NC	-90.2	-42

5

The data illustrates that a variety of donor compounds selected from aromatic ethers or a alkyl, aryl amino compounds wherein the aryl group has one or more electron withdrawing substituents including: carboxylic acids and esters, ketones, aldehydes, sulfonic acids and esters, nitriles and halogens serve as effective coinitiators for enhancing the cure speed of epoxy materials in the presence of the visible light sensitizer CPQ and DPISbF₆.

10

Example 2

The effect of an aromatic amine donor on the photopolymerization of a cycloaliphatic epoxide was evaluated. Two compositions were prepared as follows:

15

Composition A

UVR 6105	10.00 g
DPI SbF ₆	0.15 g
Camphorquinone	0.05 g
Total	10.20 g

Composition B

UVR 6105	10.00 g
DPI SbF ₆	0.15 g
Camphorquinone	0.05 g
Ethyl 4-dimethylaminobenzoate	0.025 g
Total	10.225 g

5

Each composition was prepared by combining the ingredients at room temperature and stirring until homogeneous. A drop of each composition was placed on a polyester film and irradiated with light at 400-500 nm from a Visilux light source from a distance of about 5 mm for a maximum of 60 seconds or until a tack-free material was obtained. Composition A did not cure after a 60 second exposure; Composition B was cured to a hard solid after a 15 second exposure. The composition with the electron donor EDMAB exhibited a rapid photopolymerization, whereas the composition without EDMAB failed to polymerize.

15

Example 3

The effect of various diphenyl iodonium salts was evaluated in epoxy resin compositions with and without the presence of an aromatic amine. Three epoxy containing compositions were prepared as follows:

20

Composition A(1)

UVR 6105	9.80 g
Camphorquinone	0.05 g
DPI SbF ₆	0.15 g
Total	10.00 g

Composition B(1)

UVR 6105	9.83 g
Camphorquinone	0.05 g
DPI PF ₆	0.12 g
Total	10.00 g

5 Composition C(1)

UVR 6105	9.86 g
Camphorquinone	0.05 g
DPI Cl	0.091 g
Total	10.00 g

Ethyl-p-dimethylamino benzoate was added to approximately 5 g aliquots of the above compositions:

10 Composition A(2)

Composition A(1)	4.972 g
Ethyl 4-dimethylaminobenzoate	0.028 g
Total	5.000 g

Composition B(2)

Composition B(1)	4.972 g
Ethyl 4-dimethylaminobenzoate	0.028 g
Total	5.000 g

Composition C(2)

Composition C(1)	4.972 g
Ethyl 4-dimethylaminobenzoate	0.028 g
Total	5.000 g

Each of the above compositions was prepared by combining the ingredients at room temperature and stirring until homogeneous. Each composition was evaluated for cure speed by irradiation of a 2 mm thick sample with light at a wavelength of 400-500 nm from a Visilux 2 light source at a distance of 10 mm. Irradiation continued for 120s or until a soft or hard gel was formed. Results are reported in Table 2.

Table 2

Composition	Result
A(1)	NC
B(1)	NC
C(1)	NC
A(2)	16 seconds, hard solid
B(2)	19 seconds, soft solid
C(2)	NC

The data illustrates that an epoxy composition can be rapidly photopolymerized when the amine donor EDMAB is used in combination with an iodonium salt with a PF₆ or SbF₆ counterion. No curing was observed when DPI Cl was used with or without EDMAB.

Example 4

The experiment of Example 3 was repeated using an epoxy/acrylate resin in place of the epoxy resin. The epoxy/acrylate resin was prepared by combining 45.00 g UVR 6105 and 5.00 g Ebecryl 1830 at room temperature and

stirring until homogeneous. Three epoxy/acrylate containing compositions were prepared as follows:

Composition D(1)

Epoxy/acrylate	9.80 g
Camphorquinone	0.05 g
DPI SbF ₆	0.15 g
Total	10.00 g

5

Composition E(1)

Epoxy/acrylate	9.83 g
Camphorquinone	0.05 g
DPI PF ₆	0.12 g
Total	10.00 g

Composition F(1)

Epoxy/acrylate	9.86 g
Camphorquinone	0.05 g
DPI Cl	0.09 g
Total	10.00 g

10 Ethyl 4-dimethylaminobenzoate was added to approximately 5 g aliquots of the above compositions:

Composition D(2)

Composition D(1)	4.972 g
Ethyl 4-dimethylaminobenzoate	0.028 g
Total	5.000 g

Composition E(2)

Composition E(1)	4.972 g
Ethyl 4-dimethylaminobenzoate	0.028 g
Total	5.000 g

Composition F(2)

Composition F(1)	4.972 g
Ethyl 4-dimethylaminobenzoate	0.028 g
Total	5.000 g

- 5 The irradiation time required for formation of a soft gel and/or a hard solid is reported in Table 3.

Table 3

Composition	Time to soft gel	Time to hard solid
D(1)	20 seconds (tacky)	NC
E(1)	35 seconds (tacky)	NC
F(1)	45 seconds (tacky)	NC
D(2)	5 seconds (tacky)	12 seconds
E(2)	8 seconds (tacky)	25 seconds
F(2)	8 seconds (tacky)	NC

- 10 The data shows that all of the materials initially exhibit a photopolymerization to form a soft, tacky gel indicative of a free radical methacrylate polymerization. Addition of the electron donor EDMAB results in additional cationic curing to a hard solid for compositions with DPI SbF₆ and DPI PF₆. Compositions with DPI Cl failed to cure to a hard solid with and without
- 15 EDMAB.

Example 5

The effect of varying the concentration of an amine donor compound in the photoinitiator system of the invention was investigated. A stock solution was prepared as follows:

5

Stock Solution A

UVR 6105	24.50 g
DPI SbF ₆	0.375 g
Camphorquinone	0.125 g
CH ₂ Cl ₂	0.500
Total	25.500 g

The CH₂Cl₂ was added to solubilize the catalyst. A second stock solution containing the aromatic amine EDMAB was prepared as follows:

10

Stock Solution B

UVR 6105	23.940 g
DPI SbF ₆	0.375 g
Camphorquinone	0.125 g
Ethyl 4-dimethylaminobenzoate	0.560 g
CH ₂ Cl ₂	0.500
Total	25.500 g

Again, the CH₂Cl₂ was added to solubilize the catalyst.

Sample solutions were prepared by varying the relative proportions of Stock Solution A and Stock Solution B in a 1 g sample. Each solution contained 2.9X10⁻⁵ moles of DPI SbF₆. A 2mm thick sample of each solution was irradiated with a Visilux light source at a distance of about 10 mm until a gel was obtained or for a maximum of 120 seconds. Samples were irradiated 30 minutes after mixing. Results are reported in Table 4, which show the importance of controlling the concentration of the amine donor in initiator systems of the invention.

20

Table 4

Sample Number	Grams Stock Solution A	Grams Stock Solution B	Mole Ratio		Gel Time (seconds)
			Amine:onium Salt		
1	1.0	0	0		NC
2	1.01	0.028	0.11		100 (surface skin)
3	0.96	0.07	0.29		22
4	0.9	0.1	0.41		21
5	0.8	0.2	0.83		22
6	0.7	0.3	1.20		24
7	0.6	0.4	1.59		17
8	0.5	0.5	2.00		26
9	0.4	0.6	2.40		30
10	0.3	0.7	2.80		32
11	0.2	0.8	3.20		--
12	0.1	0.9	3.60		38
13	0	1.0	4.0		90 (tacky gel)

5 Example 6

The effect of varying the concentration of an aromatic polyether donor compound in the initiator systems of the invention was investigated. Two stock solutions were prepared, one containing 1,2,4-trimethoxybenzene (TMB) as the donor and one that contained no donor:

10

Stock Solution A

UVR 6105	98.00%	9.80 gm
DPI SbF ₆	1.50%	0.15 gm
CPQ	0.50%	0.05 gm
Total	100.00%	10.0 gm

Stock Solution B

UVR 6105	93.00	9.30 gm
DPI SbF ₆	1.50%	0.15 gm
TMB	5.00%	0.50 gm
CPQ	0.50%	0.05 gm
Total	100.00%	10.00 gm

The solutions were combined in varying proportions to obtain sample solutions having various concentrations of the TMB donor. A 2 mm thick sample of each sample solution was irradiated at a distance of 10 mm using a Visilux 2 light source. The gel times are reported in Table 5.

Table 5

Sample No.	Grams Stock Solution A	Grams Stock Solution B	Molar Equivalents of TMB	Gel Time (seconds)
1	1.0	0	0	NC
2	0.975	0.026	0.26	55
3	0.95	0.058	0.0588	38
4	0.90	0.10	1.0	29
5	0.86	0.14	1.4	28
6	0.80	0.20	2.0	27
7	0.70	0.30	3.0	30
8	0.60	0.40	4.0	30
9	0.50	0.50	5.0	30
10	0.40	0.60	6.0	NT
11	0.30	0.70	7.0	33
12	0.10	0.90	9.0	34
13	0.00	1.00	10.00	38

The data illustrates that the addition of various amounts of the aromatic ether TMB results in the photopolymerization of an epoxy composition.

Example 7 (Preparative Example)

A filler composition was prepared as follows: 200.3 grams of deionized water was weighed into a 1000 ml rigid poly beaker and adjusted to a pH

of 3.02 with trifluoroacetic acid (Aldrich Chem. Co., Milwaukee, WI). 9.9099 grams of 3-glycidoxypropyltrimethoxysilane (United Chemical Technologies, Inc., Bristol, PA) was slowly added to the water while stirring with a magnetic teflon coated stirring rod. About 50 ml of denatured ethanol was used to rinse the silane addition beaker, and then added to the hydrolyzing aqueous silane solution. The solution was allowed to stir for about 65 minutes at room temperature to thoroughly hydrolyze the silane. After the 65 minutes hydrolysis time 200 grams of a 90/10 weight blend of ball mill ground mined quartz, average particle size 2.25-3.15 microns (3M Co., Maplewood, MN, PMC-41-5300-0422-9) and a commercially available fumed silica, Aerosil OX-50 (Degussa Inc., Frankfurt, GE) was slowly added to the silane treatment solution. The resulting slurry was stirred for 27 hours at room temperature. The slurry was then divided evenly among three 1000 ml poly beakers and each beaker placed in a convection drying oven for 12 hours at 60°C. The dried cake from each beaker was recombined, mortar and pestled, and then screen in a sealed container on a shaker through a 74 micron nylon screen. The screened powder was then placed in a one pint jar and dried for a final time for 2 hours at 80°C. After a short cool down the jar was then sealed with a metal cap with foil lined paper seal to reduce the moisture vapor transmission into or out of the jar.

Example 8

This Example describes the preparation of epoxy resin-based composite materials containing an iodonium salt, an alpha-diketone and an optional amine electron donor.

Two compositions were prepared as follows:

Composition A

UVR 6105	10.00 g
DPI SbF ₆	0.15 g
Camphorquinone	0.05 g
Total	10.20 g

Composition B

UVR 6105	10.00 g
DPI SbF ₆	0.15 g
Camphorquinone	0.05 g
ethyl-p-dimethylaminobenzoate	0.05 g
Total	10.20 g

Each composition was prepared by combining the ingredients at room temperature and stirring until homogeneous.

- 5 Two composite materials were further prepared by combining 7.50 grams of the filler from Example 7 with 2.50 grams of Compositions A and B respectively. Samples were spatulated until a thick homogeneous paste was obtained.

Composite A

Composition A	2.50 g
Filler from Example 7	7.50 g
Total	10.00 g

10

Composite B

Composition B	2.50 g
Filler from Example 7	7.50 g
Total	10.00 g

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Samples were evaluated for photopolymerization by determining the hardness of a 2mm thick sample according to the following procedure. A 2mm thick Teflon block which had a cylindrical hole measuring about 6 mm in diameter extending through the thickness of the block was placed on a film of transparent polyethylene terephthalate (PET) such that one end of the open cylindrical hole of the die was covered by the PET film. The Teflon die was filled with the sample and another film of PET placed on top of the die covering the sample. Hand pressure was applied to the PET film to provide an approximately 2mm thick

sample. Samples were irradiated with a Visilux 2 light source for 30 seconds by placing the light wand directly on the PET film which covered the sample at the top of the die. Three sets of samples were prepared in triplicate and stored at 25°C for 5 minutes, 20 minutes and 24 hours and at 37°C for 20 minutes and 24 hours respectively. After storage, the PET films were removed and the hardness of the top and bottom of the die was measured using a Barber-Coleman Impressor (a hand-held portable hardness tester; Model GYZJ 934-1; from Barber Coleman Company Industrial Instruments Division, Lovas Park, IN) equipped with an indenter. For each sample tested, three readings were taken at the top and bottom of each sample. The readings were averaged for each composition and storage condition. A hardness value of zero indicated limited or no polymerization. Bottom hardness values significantly less than those of the top indicate limited depth of cure. Results are summarized in Table 6 below.

Table 6

<u>Sample</u>	<u>Side Tested</u>	<u>25°C</u>			<u>37°C</u>	
		<u>5 minutes</u>	<u>20 minutes</u>	<u>24 hours</u>	<u>20 minutes</u>	<u>24 hours</u>
Composite A	Top	0	0	0	0	0
	Bottom	0	0	0	0	0
Composite B	Top	0	0	64	46	74
	Bottom	0	0	60	50	72

The data shows that composite B, which contains the donor EDMAB, exhibits significant top and bottom polymerization when post-cured for 20 or more minutes at 37°C or for 24 hrs at 25°C, whereas Composite A without EDMAB fails to exhibit significant polymerization under any of the experimental conditions.

Example 9

This Example describes the preparation of epoxy-methacrylate resin-based composite materials containing an iodonium salt, an alpha-diketone and an optional amine electron donor.

Two compositions were prepared as follows:

Composition A

UVR 6105	9.00 g
Ebecryl 1830	1.00 g
DPI SbF ₆	0.15 g
Camphorquinone	0.05 g
Total	10.20g

Composition B

UVR 6105	9.00 g
Ebecryl 1830	1.00 g
DPI SbF ₆	0.15 g
Camphorquinone	0.05 g
ethyl 4-dimethylaminobenzoate	0.05 g
Total	10.20g

5

Each composition was prepared by combining the ingredients at room temperature and stirring until homogeneous.

Two composite materials were further prepared by combining 7.50 grams of the filler from Example 7 with 2.50 grams of Compositions A and B respectively. Samples were spatulated until a thick homogeneous paste was obtained.

10

Composition A

Composition A	2.50 g
Filler from Example 7	7.50 g
Total	10.00 g

Composition B

Composition B	2.50 g
Filler from Example 7	7.50 g
Total	10.00 g

Samples were evaluated for photopolymerization by determining the hardness of a 2mm thick sample according to the procedure described in Example 8. Results are summarized in Table 7 below.

Table 7

<u>Sample</u>	<u>Side Tested</u>	<u>25°C</u>			<u>37°C</u>	
		<u>5 minutes</u>	<u>20 minutes</u>	<u>24 hours</u>	<u>20 minutes</u>	<u>24 hours</u>
Composite A	Top	0	0	0	0	0
	Bottom	0	0	0	0	0
Composite B	Top	0	0	63	45	68
	Bottom	0	0	59	38	64

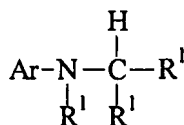
The data shows that Composite B, which contains the donor EDMAB exhibits significant top and bottom polymerization when post-cured for 20 or more minutes at 37°C or for 24 hrs at 25°C, whereas Composite A without EDMAB fails to exhibit significant polymerization under any of the experimental conditions.

The above specification, examples and data provide a complete description of the manufacture and use of the composition of the invention. The United States patents referred to in the foregoing specification are incorporated into the specification by reference. Since many embodiments of the invention can be made without departing from the spirit and scope of the invention, the invention resides in the claims hereinafter appended.

WE CLAIM:

1. A photopolymerizable composition comprising:
- (a) an epoxy resin and
- (b) a photoinitiator system comprising:
- 5 (i) an iodonium salt;
- (ii) a visible light sensitizer; and
- (iii) an electron donor compound, wherein the photoinitiator system has a photoinduced potential greater than or equal to that of 3-dimethylaminobenzoic acid in a standard solution of 2.9×10^{-5} moles/g diphenyl iodonium
- 10 hexafluoroantimonate and 1.5×10^{-5} moles/g camphorquinone in 2-butanone.

2. The composition of claim 1 wherein the donor compound is described by the following structural formula:



- 15 wherein R^1 are independently H, C_{1-18} alkyl that is optionally substituted by one or more halogen, -CN, -OH, -SH, C_{1-18} alkoxy, C_{1-18} alkylthio, C_{3-18} cycloalkyl, aryl, COOH , COOC_{1-18} alkyl, $(\text{C}_{1-18} \text{ alkyl})_{0-1}-\text{CO}-\text{C}_{1-18}$ alkyl, SO_3H , CN or halogen groups, or aryl that is optionally substituted by one or more electron withdrawing
- 20 groups where R^2 is H, C_{1-18} alkyl that is optionally substituted by one or more halogen, -CN, -OH, -SH, C_{1-18} alkoxy, C_{1-18} alkylthio, C_{3-18} cycloalkyl, aryl, COOH , COOC_{1-18} alkyl, $(\text{C}_{1-18} \text{ alkyl})_{0-1}-\text{CO}-\text{C}_{1-18}$ alkyl, SO_3H , CN or halogen groups, or aryl that is optionally substituted by one or more electron withdrawing groups, or the
- 25 R^1 groups together may form a ring; and Ar is aryl that is substituted by one or more electron withdrawing groups.

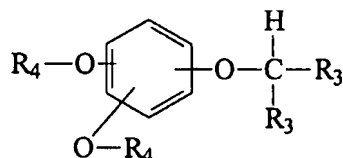
3. The composition of claim 2 wherein the aryl group is substituted by one or more carboxylic acid, carboxylic acid ester, ketone, aldehyde, sulfonic acid, sulfonate, or nitrile groups.

4. The composition of claim 2 wherein the aryl group is substituted by one or more moieties selected from the group consisting of -COOH, -COOC₁₋₁₈ alkyl, -SO₃R², -CN, -CO-C₁₋₁₈ alkyl and -C(O)H groups, where R² is H, C₁₋₁₈ alkyl that is optionally substituted by one or more halogen, -CN, -OH, -SH, C₁₋₁₈ alkoxy, C₁₋₁₈ alkylthio, C₃₋₁₈ cycloalkyl, aryl, COOH, COOC₁₋₁₈ alkyl, (C₁₋₁₈ alkyl)₀₋₁-CO-C₁₋₁₈ alkyl, SO₃H, CN or halogen groups, or aryl that is optionally substituted by one or more electron withdrawing groups.

5. The composition of claim 1 wherein the donor compound is selected from the group consisting of 4-dimethylaminobenzoic acid, ethyl 4-dimethylaminobenzoate, 3-dimethylaminobenzoic acid, 4-dimethylaminobenzoin, 4-dimethylaminobenzaldehyde, 4-dimethylaminobenzonitrile and 1,2,4-trimethoxybenzene.

6. The composition of claim 1 wherein the donor compound is an alkyl, aryl polyether.

7. The composition of claim 1 wherein the donor compound is an alkyl, aryl polyether having the structural formula:



wherein n = 1-3 each R₃ is independently H or C₁₋₁₈ alkyl that is optionally substituted by one or more halogen, -CN, -OH, -SH, C₁₋₁₈ alkoxy, C₁₋₁₈ alkylthio, C₃₋₁₈ cycloalkyl, aryl, substituted aryl, -COOH, -COOC₁₋₁₈ alkyl, -(C₁₋₁₈ alkyl)₀₋₁-COH, -(C₁₋₁₈ alkyl)₀₋₁-CO-C₁₋₁₈ alkyl, -CO-C₁₋₁₈ alkyl, -C(O)H or -C₂₋₁₈ alkenyl groups, or the R₃ groups together may form a ring and each R₄ can be C₁₋₁₈ alkyl that is optionally substituted by one or more halogen, -CN, -OH, -SH, C₁₋₁₈ alkoxy, C₁₋₁₈ alkylthio, C₃₋₁₈ cycloalkyl, aryl, substituted aryl, -COOH, -COOC₁₋₁₈ alkyl, -

(C₁₋₁₈ alkyl)₀₋₁-COH, -(C₁₋₁₈ alkyl)₀₋₁-CO-C₁₋₁₈ alkyl, -CO-C₁₋₁₈ alkyl, -C(O)H or -C₂₋₁₈ alkenyl groups.

5 8. The composition of claim 1 wherein the iodonium salt is an aryl iodonium salt.

 9. The composition of claim 1 wherein the iodonium salt comprises diphenyliodonium chloride, diphenyl iodonium hexafluorophosphate, diphenyl iodonium hexafluoroantimonate, diphenyl iodonium tetrafluoroborate, or
10 a mixture thereof.

 10. The composition of claim 1 wherein the sensitizing compound comprises a ketone.

15 11. The composition of claim 1 wherein the sensitizing compound comprises an aliphadiketone.

 12. The composition of claim 1 wherein the sensitizing compound comprises a ketocoumarin, aminoarylketone, or a para-substituted
20 aminostyrylketone compound.

 13. The composition of claim 1 wherein the sensitizing compound comprises camphorquinone.

25 14. The composition of claim 1 wherein the composition cures to a tack-free gel within 60 seconds after exposure to visible light.

 15. The composition of claim 1 wherein the epoxy resin comprises a cycloaliphatic epoxide or diepoxide.
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16. The composition of claim 1 wherein the epoxy resin comprises a bisphenol-A diepoxide.

17. The composition of claim 1 wherein the epoxy resin contains ethylenic unsaturation.

18. The composition of claim 1 further comprising an ethylenically unsaturated compound.

19. The composition of claim 16 wherein the ethylenically unsaturated compound is an ester of acrylic acid or methacrylic acid.

20. The composition of claim 16 wherein the ethylenically unsaturated compound comprises methyl acrylate, methyl methacrylate, ethyl acrylate, isopropyl methacrylate, n-hexyl acrylate, stearyl acrylate, allyl acrylate, glycerol diacrylate, glycerol triacrylate, ethyleneglycol diacrylate, diethyleneglycol diacrylate, triethyleneglycol dimethacrylate, 1,3-propanediol diacrylate, 1,3-propanediol dimethacrylate, trimethylolpropane triacrylate, 1,2,4-butanetriol trimethacrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, sorbitol hexacrylate or a mixture thereof.

21. A photopolymerizable composition comprising:

(a) an epoxy resin;

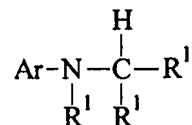
(b) a photoinitiator system comprising:

(i) a diaryliodonium hexafluoroantimonate or diaryliodonium hexafluorophosphate;

(ii) camphorquinone and

(iii) an electron donor described by the following structural

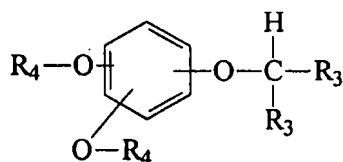
formula:



wherein R^1 are independently H, C_{1-18} alkyl that is optionally substituted by one or more halogen, -CN, -OH, -SH, C_{1-18} alkoxy, C_{1-18} alkylthio, C_{3-18} cycloalkyl, aryl, COOH, COOC_{1-18} alkyl, $(\text{C}_{1-18} \text{ alkyl})_{0-1}$ -CO- C_{1-18} alkyl, SO_3H , CN or halogen groups, or aryl that is optionally substituted by one or more electron withdrawing groups where R^2 is H, C_{1-18} alkyl that is optionally substituted by one or more halogen, -CN, -OH, -SH, C_{1-18} alkoxy, C_{1-18} alkylthio, C_{3-18} cycloalkyl, aryl, COOH, COOC_{1-18} alkyl, $(\text{C}_{1-18} \text{ alkyl})_{0-1}$ -CO- C_{1-18} alkyl, SO_3H , CN or halogen groups, or aryl that is optionally substituted by one or more electron withdrawing groups, or the R^1 groups together may form a ring; and Ar is aryl that is substituted by one or more electron withdrawing groups.

22. A photopolymerizable composition comprising:

- (a) an epoxy resin;
- (b) a photoinitiator system comprising:
 - (i) a diaryliodonium hexafluoroantimonate or diaryliodonium hexafluorophosphate;
 - (ii) camphorquinone and
 - (iii) an electron donor described by the following structural formula:



wherein $n = 1-3$ each R_3 is independently H or C_{1-18} alkyl that is optionally substituted by one or more halogen, -CN, -OH, -SH, C_{1-18} alkoxy, C_{1-18} alkylthio, C_{3-18} cycloalkyl, aryl, substituted aryl, -COOH, - COOC_{1-18} alkyl, $-(\text{C}_{1-18} \text{ alkyl})_{0-1}$ -COH, $-(\text{C}_{1-18} \text{ alkyl})_{0-1}$ -CO- C_{1-18} alkyl, -CO- C_{1-18} alkyl, -C(O)H or - C_{2-18} alkenyl groups, or the R^3 groups together may form a ring and each R_4 can be C_{1-18} alkyl

that is optionally substituted by one or more halogen, -CN, -OH, -SH, C₁₋₁₈ alkoxy, C₁₋₁₈ alkylthio, C₃₋₁₈ cycloalkyl, aryl, substituted aryl, -COOH, -COOC₁₋₁₈ alkyl, -(C₁₋₁₈ alkyl)₀₋₁-COH, -(C₁₋₁₈ alkyl)₀₋₁-CO-C₁₋₁₈ alkyl, -CO-C₁₋₁₈ alkyl, -C(O)H or -C₂₋₁₈ alkenyl groups.

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23. A method for photopolymerization comprising the step of irradiating a photopolymerizable composition with light having a wavelength between about 400 and 1000 nanometers until said composition gels or hardens, said composition comprising:

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- (a) an epoxy resin;
- (b) a photoinitiator system, said photoinitiator system comprising:
 - (i) an iodonium salt;
 - (ii) a visible light sensitizer; and
 - (iii) an electron donor compound, wherein the photoinitiator

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system has a photoinduced potential of at least about 100mV relative to a standard solution of 2.9×10^{-5} moles per gram diphenyliodonium hexafluoroantimonate and 1.5×10^{-5} moles per gram camphorquinone in 2-butanone.

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24. The method of claim 23 wherein the composition additionally comprises an ethylenically unsaturated compound.

25. A photopolymerizable dental composition comprising:

25

- (a) an epoxy resin;
- (b) a photoinitiator system comprising:
 - (i) an iodonium salt;
 - (ii) a visible light sensitizer; and
 - (iii) an electron donor compound, wherein the photoinitiator

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system has a photoinduced potential of at least about 100mV relative to a standard solution of 2.9×10^{-5} moles/g diphenyl iodonium hexafluoroantimonate and 1.5×10^{-5} moles/g camphorquinone in 2-butanone.

26. A composition of claim 25, wherein said composition is a dental adhesive.

5 27. A composition of claim 25, wherein said composition is a dental composite material.

28. A composition of claim 25, wherein said composition is a dental sealant.

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29. A composition of claim 25, wherein said composition is an orthodontic adhesive.

15 30. A composition of claim 1, wherein said composition is a graphic arts imaging composition.

31. A composition of claim 1, wherein said composition is selected from the group consisting of photoresists, solder masks, electronic conformal coatings, coated abrasives and magnetic media compositions.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/04029

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 G03F7/038 G03F7/029 A61K6/087 A61K6/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G03F C08G A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 13538 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 9 May 1996 cited in the application see page 31, line 3 - line 20 ---	1-31
A	EP 0 290 133 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 9 November 1988 cited in the application * page 7, run no. 21, 25 and 31 * -----	1-31

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☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9613538 A	09-05-1996	AU 3971895 A EP 0789721 A	23-05-1996 20-08-1997
EP 0290133 A	09-11-1988	CA 1323949 A JP 2744789 B JP 63273602 A US 5545676 A	02-11-1993 28-04-1998 10-11-1988 13-08-1996

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(51) International Patent Classification ⁶ : G03F 7/038, 7/029, A61K 6/087, 6/00	A1	(11) International Publication Number: WO 98/47047 (43) International Publication Date: 22 October 1998 (22.10.98)
(21) International Application Number: PCT/US98/04458 (22) International Filing Date: 6 March 1998 (06.03.98) (30) Priority Data: 08/840,093 11 April 1997 (11.04.97) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: OXMAN, Joel, D.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). JACOBS, Dwight, W.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: BJORKMAN, Dale, A. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: TERNARY PHOTOINITIATOR SYSTEM FOR CURING OF EPOXY/POLYOL RESIN COMPOSITIONS (57) Abstract Photocurable, addition polymerizable compositions contain an epoxy resin and a photoinitiator system containing (a) an epoxy resin, (b) a hydroxyl containing material and (c) a photoinitiator system comprising: (i) an iodonium salt; (ii) a visible light sensitizer; and (iii) an electron donor compound, wherein the photoinitiator system has a photoinduced potential of at least about 100 mV relative to a standard solution of 2.9×10^{-5} moles/g diphenyl iodonium hexafluoroantimonate and 1.5×10^{-5} moles/g camphorquinone in 2-butanone. The compositions cure on exposure to light in the visible spectrum and are useful in a variety of applications, including dental adhesives and composites.		

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BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
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BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
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CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
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DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Ternary Photoinitiator System
for Curing of Epoxy/Polyol Resin Compositions

Field of the Invention

5 The invention relates to photocurable, addition polymerizable compositions that contain an epoxy resin, a hydroxyl containing material, and optionally a free radically polymerizable material. The compositions contain a ternary photoinitiator system that is activated on exposure to actinic radiation in the visible spectrum. The invention is additionally directed to methods of curing
10 addition polymerizable compositions using the ternary photoinitiator system.

Background of the Invention

 Epoxy containing compounds are known to be curable using various cationic initiator systems. Smith, in U.S. Patent No. 4,256,828, describes photopolymerizable compositions that contain epoxides, an organic compound
15 with hydroxyl functionality, and a photosensitive aromatic sulfonium or iodonium salt of a halogen containing complex ion. Hayase et al., U.S. Patent No. 4,835,193, describes photopolymerizable epoxy resin compositions that comprise an epoxy resin and a heteropoly-acid aromatic sulfonium salt as the photocuring catalyst. In WO 95/14716 Neckers et al. describe photohardenable compositions that comprise
20 a cationically polymerizable compound, a xanthene or fluorone dye, a hydrogen donor, and an onium salt. Palazzotto et al., U.S. Patent No. 5,545,676, describes addition polymerization of free-radically polymerizable materials. The photoinitiator system described in that patent comprises an aryliodonium salt, a sensitizer, and an electron donor having an oxidation potential less than or equal to
25 that of p-dimethoxybenzene.

 PCT published application No. WO 96/13538 describes a system for curing epoxy compounds by exposure to visible light by use of a system comprising an aryliodonium salt and a sensitizer. Comparative Example 34 of this disclosure describes the use of one of the initiator systems of Palazzotto et al., U.S.
30 Patent No. 5,545,676 in an epoxy/polyol resin system. N, N-dimethylbenzylamine

is used as the electron donor. The results of this experiment indicated that the use of this amine donor tended to retard the cure of the resin system.

Suppliers of cationically cured resins expressly warn against using organic amines in photoinitiated epoxy resins. An example of such a warning is found in Union Carbide literature regarding Cyracure® cycloaliphatic epoxides.

Summary of the Invention

We have discovered, and the invention provides, a photopolymerizable composition that contains an epoxy resin, a hydroxyl-functional compound and a photoinitiator system containing an iodonium salt, a visible light sensitizer, and an electron donor compound, wherein the photoinitiator system has a photoinduced potential greater than or equal to that of 3-dimethylamino benzoic acid in a standard solution of 2.9×10^{-5} moles/g diphenyl iodonium hexafluoroantimonate and 1.5×10^{-5} moles/g camphorquinone in 2-butanone. Generally, 3-dimethylamino benzoic acid in this standard exhibits a photoinduced potential of at least about 115mV relative to a standard solution of 2.9×10^{-5} moles/g diphenyl iodonium hexafluoroantimonate and 1.5×10^{-5} moles/g camphorquinone in 2-butanone.

These compositions are curable on exposure to light having a wavelength of about 400 to 1000 nm, and the invention provides a method of addition photopolymerization comprising the step of irradiating a photopolymerizable composition with light having a wavelength of about 400 to 1000 nm until the composition gels or hardens, the composition containing an epoxy resin, a hydroxyl-containing material and a photoinitiator system containing an iodonium salt, a visible light sensitizer, and an electron donor compound wherein the photoinitiator system has a photoinduced potential of at least about 100mV relative to a standard solution of 2.9×10^{-5} moles/g diphenyl iodonium hexafluoroantimonate and 1.5×10^{-5} moles/g camphorquinone in 2-butanone.

In this application "polyol" and "hydroxyl-containing material" are used interchangeably.

The initiator systems of the invention allow efficient cationic polymerization under conditions of room temperature and standard pressure. In

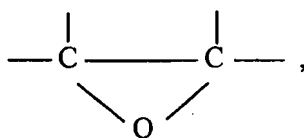
addition, the initiator systems can, under appropriate conditions, initiate both cationic and free-radical polymerization. This property permits their use with a variety of photopolymerizable compositions, including systems that contain acrylate or methacrylate functionality. Use of the initiator systems of the invention can provide a substantial reduction in the time required for an epoxy and hydroxyl containing resin composition to cure to a tack-free gel or solid. This reduction in gel time can represent about a 30 to 70% decrease in the time required for a resin composition to harden to a tack-free gel or solid.

Detailed Description of the Invention

The photopolymerizable compositions of the invention are sensitive throughout the visible spectral region and photocure without the need to introduce substantial heat to the system to initiate cure, although an incidental amount of heat can be present. The term "visible light" is used throughout this application to refer to light having a wavelength of about 400 to 1000 nanometers (nm).

Photopolymerization of the compositions takes place on exposure of the compositions to a source of actinic radiation having a wavelength within this spectral region.

The cationically polymerizable epoxy resins useful in the compositions of the invention are organic compounds having an oxirane ring, i.e., a group of the formula



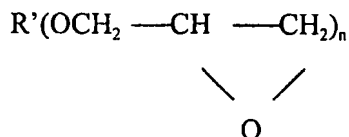
which is polymerizable by ring opening. Such materials, broadly called epoxides, include monomeric epoxy compounds and epoxides of the polymeric type and can be aliphatic, cycloaliphatic, aromatic or heterocyclic. These materials generally have, on the average, at least 1 polymerizable epoxy group per molecule, preferably at least about 1.5 and more preferably at least about 2 polymerizable epoxy groups per molecule. The polymeric epoxides include linear polymers

having terminal epoxy groups (e.g., a diglycidyl ether of a polyoxyalkylene glycol), polymers having skeletal oxirane units (e.g., polybutadiene polyepoxide), and polymers having pendent epoxy groups (e.g., a glycidyl methacrylate polymer or copolymer). The epoxides may be pure compounds or may be mixtures of compounds containing one, two, or more epoxy groups per molecule. The "average" number of epoxy groups per molecule is determined by dividing the total number of epoxy groups in the epoxy-containing material by the total number of epoxy-containing molecules present.

These epoxy-containing materials may vary from low molecular weight monomeric materials to high molecular weight polymers and may vary greatly in the nature of their backbone and substituent groups. For example, the backbone may be of any type and substituent groups thereon can be any group that does not substantially interfere with cationic cure at room temperature. Illustrative of permissible substituent groups include halogens, ester groups, ethers, sulfonate groups, siloxane groups, nitro groups, phosphate groups, and the like. The molecular weight of the epoxy-containing materials may vary from about 58 to about 100,000 or more.

Useful epoxy-containing materials include those which contain cyclohexene oxide groups such as epoxycyclohexanecarboxylates, typified by 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate, 3,4-epoxy-2-methylcyclohexylmethyl-3,4-epoxy-2-methylcyclohexane carboxylate, and bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate. For a more detailed list of useful epoxides of this nature, reference is made to the U.S. Patent No. 3,117,099, which is incorporated herein by reference.

Further epoxy-containing materials which are useful in the compositions of this invention include glycidyl ether monomers of the formula



where R' is alkyl or aryl and n is an integer of 1 to 6. Examples are glycidyl ethers of polyhydric phenols obtained by reacting a polyhydric phenol with an excess of chlorohydrin such as epichlorohydrin (e.g., the diglycidyl ether of 2,2-bis-(2,3-epoxypropoxyphenol)-propane). Further examples of epoxides of this type are
5 described in U.S. Patent No. 3,018,262, which is incorporated herein by reference, and in "Handbook of Epoxy Resins" by Lee and Neville, McGraw-Hill Book Co., New York (1967).

There are a host of commercially available epoxy resins which can be used in this invention. In particular, epoxides which are readily available
10 include octadecylene oxide, epichlorohydrin, styrene oxide, vinyl cyclohexene oxide, glycidol, glycidylmethacrylate, diglycidyl ether of Bisphenol A (e.g., those available under the trade designations "Epon 828", "Epon 825", "Epon 1004" and "Epon 1010" from Shell Chemical Co., "DER-331", "DER-332", and "DER-334", from Dow Chemical Co.), vinylcyclohexene dioxide (e.g., "ERL-4206" from
15 Union Carbide Corp.), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexene carboxylate (e.g., "ERL-4221" or "CYRACURE UVR 6110" or UVR 6105" from Union Carbide Corp.), 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexene carboxylate (e.g., "ERL-4201" from Union Carbide Corp.), bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate (e.g., "ERL-4289" from Union Carbide
20 Corp.), bis(2,3-epoxycyclopentyl) ether (e.g., "ERL-0400" from Union Carbide Corp.), aliphatic epoxy modified from polypropylene glycol (e.g., "ERL-4050" and "ERL-4052" from Union Carbide Corp.), dipentene dioxide (e.g., "ERL-4269" from Union Carbide Corp.), epoxidized polybutadiene (e.g., "Oxiron 2001" from FMC Corp.), silicone resin containing epoxy functionality, flame retardant epoxy
25 resins (e.g., "DER-580", a brominated bisphenol type epoxy resin available from Dow Chemical Co.), 1,4-butanediol diglycidyl ether of phenolformaldehyde novolak (e.g., "DEN-431" and "DEN-438" from Dow Chemical Co.), and resorcinol diglycidyl ether (e.g., "Kopoxite" from Koppers Company, Inc.), bis(3,4-epoxycyclohexyl)adipate (e.g., "ERL-4299" or "UVR-6128", from Union
30 Carbide Corp.), 2-(3,4-epoxycyclohexyl-5, 5-spiro-3,4-epoxy) cyclohexane-metadioxane (e.g., "ERL-4234" from Union Carbide Corp.), vinylcyclohexene

monoxide 1,2-epoxyhexadecane (e.g., "UVR-6216" from Union Carbide Corp.), alkyl glycidyl ethers such as alkyl C₈-C₁₀ glycidyl ether (e.g., "HELOXY Modifier 7" from Shell Chemical Co.), alkyl C₁₂-C₁₄ glycidyl ether (e.g., "HELOXY Modifier 8" from Shell Chemical Co.), butyl glycidyl ether (e.g., "HELOXY Modifier 61" from Shell Chemical Co.), cresyl glycidyl ether (e.g., "HELOXY Modifier 62" from Shell Chemical Co.), p-ter butylphenyl glycidyl ether (e.g., "HELOXY Modifier 65" from Shell Chemical Co.), polyfunctional glycidyl ethers such as diglycidyl ether of 1,4-butanediol (e.g., "HELOXY Modifier 67" from Shell Chemical Co.), diglycidyl ether of neopentyl glycol (e.g., "HELOXY Modifier 68" from Shell Chemical Co.), diglycidyl ether of cyclohexanedimethanol (e.g., "HELOXY Modifier 107" from Shell Chemical Co.), trimethylol ethane triglycidyl ether (e.g., "HELOXY Modifier 44" from Shell Chemical Co.), trimethylol propane triglycidyl ether (e.g., "HELOXY Modifier 48" from Shell Chemical Co.), polyglycidyl ether of an aliphatic polyol (e.g., "HELOXY Modifier 84" from Shell Chemical Co.), polyglycol diepoxide (e.g., "HELOXY Modifier 32" from Shell Chemical Co.), bisphenol F epoxides (e.g., "EPN-1138" or "GY-281" from Ciba-Geigy Corp.), 9,9-bis[4-(2,3-epoxypropoxy)-phenyl]fluorenone (e.g., "Epon 1079" from Shell Chemical Co.).

Still other epoxy resins contain copolymers of acrylic acid esters or glycidol such as glycidylacrylate and glycidylmethacrylate with one or more copolymerizable vinyl compounds. Examples of such copolymers are 1:1 styrene-glycidylmethacrylate, 1:1 methylmethacrylate-glycidylacrylate and a 62.5:24:13.5 methylmethacrylate-ethyl acrylate-glycidylmethacrylate.

Other useful epoxy resins are well known and contain such epoxides as epichlorohydrins, alkylene oxides, e.g., propylene oxide, styrene oxide; alkenyl oxides, e.g., butadiene oxide; glycidyl esters, e.g., ethyl glycidate.

The polymers of the epoxy resin can optionally contain other functionalities that do not substantially interfere with cationic cure at room temperature.

Blends of various epoxy-containing materials are also contemplated in this invention. Examples of such blends include two or more weight average

molecular weight distributions of epoxy-containing compounds, such as low molecular weight (below 200), intermediate molecular weight (about 200 to 10,000) and higher molecular weight (above about 10,000). Alternatively or additionally, the epoxy resin may contain a blend of epoxy-containing materials having different chemical natures, such as aliphatic and aromatic, or functionalities, such as polar and non-polar. Other cationically polymerizable polymers can additionally be incorporated, such as vinyl ethers, etc., if desired.

The hydroxyl-containing material which is used in the present invention can be any organic material having hydroxyl functionality of at least 1, and preferably at least 2.

Preferably the hydroxyl-containing material contains two or more primary or secondary aliphatic hydroxyl groups (i.e., the hydroxyl group is bonded directly to a non-aromatic carbon atom). The hydroxyl groups can be terminally situated, or they can be pendent from a polymer or copolymer. The molecular weight of the hydroxyl-containing organic material can vary from very low (e.g., 32) to very high (e.g., one million or more). Suitable hydroxyl-containing materials can have low molecular weights, i.e. from about 32 to 200, intermediate molecular weight, i.e. from about 200 to 10,000, or high molecular weight, i.e. above about 10,000. As used herein, all molecular weights are weight average molecular weights.

The hydroxyl-containing material can optionally contain other functionalities that do not substantially interfere with cationic cure at room temperature. Thus, the hydroxyl-containing materials can be nonaromatic in nature or can contain aromatic functionality. The hydroxyl-containing material can optionally contain heteroatoms in the backbone of the molecule, such as nitrogen, oxygen, sulfur, and the like, provided that the ultimate hydroxyl-containing material does not substantially interfere with cationic cure at room temperature. The hydroxyl-containing material can, for example, be selected from naturally occurring or synthetically prepared cellulosic materials. Of course, the hydroxyl-containing material is also substantially free of groups which may be thermally or photolytically unstable; that is, the material will not decompose or liberate volatile

components at temperatures below about 100°C or in the presence of actinic light which may be encountered during the desired curing conditions for the photocopolymerizable composition.

Representative examples of suitable hydroxyl-containing materials having a hydroxyl functionality of 1 include alkanols, monoalkyl ethers of polyoxyalkyleneglycols, monoalkyl ethers of alkylene-glycols, and others known in the art.

Representative examples of useful monomeric polyhydroxy organic materials include alkylene glycols (e.g., 1,2-ethanediol; 1,3-propanediol; 1,4-butanediol; 1,6-hexanediol; 1,8-octanediol; 2-ethyl-1,6-hexanediol; bis(hydroxymethyl)cyclohexane; 1,18-dihydroxyoctadecane; 3-chloro-1,2-propanediol); polyhydroxyalkanes (e.g., glycerine, tri-methylolethane, pentaerythritol, sorbitol) and other polyhydroxy compounds such as N,N-bis(hydroxyethyl)benzamide; 2-butyne-1,4-diol; 4,4-bis(hydroxymethyl)diphenylsulfone; castor oil; and the like.

Representative examples of useful polymeric hydroxyl-containing materials include polyoxyethylene and polyoxypropylene glycols, and particularly the polyoxyethylene and polyoxypropylene glycol diols and triols having molecular weights from about 200 to about 10,000 corresponding to a hydroxy equivalent weight of 100 to 5000 for the diols or 70 to 3300 for triols; polytetramethylene ether glycols such as polytetrahydrofuran or "poly THF" of varying molecular weight; copolymers of hydroxypropyl and hydroxyethyl acrylates and methacrylates with other free radical-polymerizable monomers such as acrylate esters, vinyl halides, or styrene; copolymers containing pendent hydroxy groups formed by hydrolysis or partial hydrolysis of vinyl acetate copolymers, polyvinylacetal resins containing pendent hydroxyl groups; modified cellulose polymers such as hydroxyethylated and hydroxypropylated cellulose; hydroxy-terminated polyesters; hydroxy-terminated polylactones, and particularly the polycaprolactones; fluorinated polyoxyethylene or polyoxypropylene glycols; and hydroxy-terminated polyalkadienes.

Useful commercially available hydroxyl-containing materials include the "TERATHANE" series of polytetramethylene ether glycols such as "TERATHANE" 650, 1000, 2000 and 2900 (available from du Pont de Nemours, Wilmington, DE) the "PEP" series of polyoxyalkylene tetrols having secondary hydroxyl groups such as "PEP" 450, 550 and 650; "BUTVAR" series of polyvinylacetal resins such as "BUTVAR" B-72A, B-73, B-76, B-90 and B-98 (available from Monsanto Chemical Company, St. Louis, MO); and the "FORMVAR" series of resins such as 7/70, 12/85, 7/95S, 7/95E, 15/95S and 15/95E (available from Monsanto Chemical Company); the "TONE" series of polycaprolactone polyols such as "TONE" 0200, 0210, 0230, 0240, 0300 and 0301 (available from Union Carbide); "PARAPLEX U-148" aliphatic polyester diol (available from Rohm and Haas, Philadelphia, PA), the "MULTRON" R series of saturated polyester polyols such as "MULTRON" R-2, R-12A, R-16, R-18, R-38, R-68 and R-74 (available from Mobay Chemical Co.); "KLUCEL E" hydroxypropylated cellulose having an equivalent weight of approximately 100 (available from Hercules Inc.); "Alcohol Soluble Butyrate" cellulose acetate butyrate ester having a hydroxyl equivalent weight of approximately 400 (available from Eastman Kodak Co., Rochester, NY); polyether polyols such as polypropylene glycol diol (e.g., "ARCOL PPG-425", "Arcol PPG-725", "ARCOL PPG-1025", "ARCOL PPG-2025", "ARCOL PPG-3025", "ARCOL PPG-4025" from ARCO Chemical Co.); polypropylene glycol triol (e.g., "ARCOL LT-28", "ARCOL LHT-42", "ARCOL LHT 112", "ARCOL LHT 240", "ARCOL LG-56", "ARCOL LG-168", "ARCOL LG-650" from ARCO Chemical Co.); ethylene oxide capped polyoxypropylene triol or diol (e.g., "ARCOL 11-27", "ARCOL 11-34", "ARCOL E-351", "ARCOL E-452", "ARCOL E-785", "ARCOL E-786" from ARCO Chemical Co.); ethoxylated bis-phenol A; propylene oxide or ethylene oxide - based polyols (e.g., "VORANOL" polyether polyols from the Dow Chemical Co.).

The amount of hydroxyl-containing organic material used in the compositions of the invention may vary over broad ranges, depending upon factors such as the compatibility of the hydroxyl-containing material with the epoxide, the

equivalent weight and functionality of the hydroxyl-containing material, the physical properties desired in the final cured composition, the desired speed of photocure, and the like.

5 Blends of various hydroxyl-containing materials are particularly contemplated in this invention. Examples of such blends include two or more molecular weight distributions of hydroxyl-containing compounds, such as low molecular weight (below 200), intermediate molecular weight (about 200 to 10,000) and higher molecular weight (above about 10,000). Alternatively or additionally, the hydroxyl-containing material can contain a blend of hydroxyl-
10 containing materials having different chemical natures, such as aliphatic and aromatic, or functionalities, such as polar and non-polar. As an additional example, one may use mixtures of two or more poly-functional hydroxy materials or one or more mono-functional hydroxy materials with poly-functional hydroxy materials.

15 If desired, the composition can also contain a free-radically polymerizable material, including one or more ethylenically unsaturated monomer, monomers, oligomers or polymers. Suitable materials contain at least one ethylenically unsaturated bond, and are capable of undergoing addition polymerization. Such free radically polymerizable materials include mono-, di- or
20 poly- acrylates and methacrylates such as methyl acrylate, methyl methacrylate, ethyl acrylate, isopropyl methacrylate, n-hexyl acrylate, stearyl acrylate, allyl acrylate, glycerol diacrylate, glycerol triacrylate, ethyleneglycol diacrylate, diethyleneglycol diacrylate, triethyleneglycol dimethacrylate, 1,3-propanediol diacrylate, 1,3-propanediol dimethacrylate, trimethylolpropane triacrylate, 1,2,4-
25 butanetriol trimethacrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, sorbitol hexacrylate, bis[1-(2-acryloxy)]-p-ethoxyphenyldimethylmethane, bis[1-(3-acryloxy-2-hydroxy)]-p-propoxyphenyldimethylmethane, and trishydroxyethyl-
isocyanurate trimethacrylate; the bis-acrylates and bis-methacrylates of
30 polyethylene glycols of molecular weight 200-500, copolymerizable mixtures of acrylated monomers such as those in U.S. Pat. No. 4,652,274, and acrylated

oligomers such as those of U.S. Pat. No. 4,642,126; and vinyl compounds such as styrene, diallyl phthalate, divinyl succinate, divinyl adipate and divinylphthalate. Mixtures of two or more of these free radically polymerizable materials can be used if desired.

5 If desired, the polymerizable material(s) may contain both epoxy and free-radically polymerizable functionalities in a single molecule. These may be obtained by reacting a di- or poly-epoxide with one or more equivalents of an ethylenically unsaturated carboxylic acid. An example of such a material is the reaction product of UVR-6105 (available from Union Carbide) with one equivalent
10 of methacrylic acid. Commercially available materials having epoxy and free-radically polymerizable functionalities include the "Cyclomer" series, such as Cyclomer M100 or M101, available from Daicel Chemical, Japan.

 The polymerizable material(s) can also contain hydroxyl and free radically polymerizable functionalities in a single molecule. Examples of such
15 materials include hydroxyalkylacrylates and hydroxyalkylmethacrylates such as hydroxyethylacrylate, hydroxyethylmethacrylate; glycerol mono- or di-acrylate and methacrylate; and the like.

 The epoxy resin, hydroxyl-containing material and optional free radically polymerizable material(s) are combined with a three component or
20 ternary photoinitiator system. Three component initiator systems are described in Palazzotto et al., U.S. Patent No. 5,545,676, which is incorporated herein by reference. The first component in the photoinitiator system is an iodonium salt, i.e., a diaryliodonium salt. The iodonium salt should be soluble in the monomer and preferably is shelf-stable, meaning it does not spontaneously promote
25 polymerization when dissolved therein in the presence of the sensitizer and donor. Accordingly, selection of a particular iodonium salt may depend to some extent upon the particular monomer, sensitizer and donor chosen. Suitable iodonium salts are described in U.S. Pat. Nos. 3,729,313, 3,741,769, 3,808,006, 4,250,053 and 4,394,403, the iodonium salt disclosures of which are incorporated herein by
30 reference. The iodonium salt can be a simple salt, containing an anion such as Cl⁻, Br⁻, I⁻ or C₄H₉SO₃⁻; or a metal complex salt containing an antimonate, arsenate,

phosphate or borate such as SbF_6^- or AsF_6^- . Mixtures of iodonium salts can be used if desired.

Examples of useful aromatic iodonium complex salt photoinitiators include: diphenyliodonium tetrafluoroborate; di(4-methylphenyl)iodonium tetrafluoroborate; phenyl-4-methylphenyliodonium tetrafluoroborate; di(4-heptylphenyl)iodonium tetrafluoroborate; di(3-nitrophenyl)iodonium hexafluorophosphate; di(4-chlorophenyl)iodonium hexafluorophosphate; di(naphthyl)iodonium tetrafluoroborate; di(4-trifluoromethylphenyl)iodonium tetrafluoroborate; diphenyliodonium hexafluorophosphate; di(4-methylphenyl)iodonium hexafluorophosphate; diphenyliodonium hexafluoroarsenate; di(4-phenoxyphenyl)iodonium tetrafluoroborate; phenyl-2-thienyliodonium hexafluorophosphate; 3,5-dimethylpyrazolyl-4-phenyliodonium hexafluorophosphate; diphenyliodonium hexafluoroantimonate; 2,2'-diphenyliodonium tetrafluoroborate; di(2,4-dichlorophenyl)iodonium hexafluorophosphate; di(4-bromophenyl)iodonium hexafluorophosphate; di(4-methoxyphenyl)iodonium hexafluorophosphate; di(3-carboxyphenyl)iodonium hexafluorophosphate; di(3-methoxycarbonylphenyl)iodonium hexafluorophosphate; di(3-methoxysulfonylphenyl)iodonium hexafluorophosphate; di(4-acetamidophenyl)iodonium hexafluorophosphate; di(2-benzothienyl)iodonium hexafluorophosphate; and diphenyliodonium hexafluoroantimonate.

Of the aromatic iodonium complex salts which are suitable for use in the compositions of the invention diaryliodonium hexafluorophosphate and diaryliodonium hexafluoroantimonate are among the preferred salts. These salts are preferred because, in general, they promote faster reaction, and are more soluble in inert organic solvents than are other aromatic iodonium salts of complex ions.

The aromatic iodonium complex salts may be prepared by metathesis of corresponding aromatic iodonium simple salts (such as, for example, diphenyliodonium bisulfate) in accordance with the teachings of Beringer et al., J. Am. Chem. Soc. 81,342 (1959). Thus, for example, the complex salt diphenyliodonium tetrafluoroborate is prepared by the addition at 60°C of an

aqueous solution containing 29.2 g silver fluoroborate, 2 g fluoroboric acid, and 0.5 g phosphorous acid in about 30 ml of water to a solution of 44 g (139 millimoles) of diphenyliodonium chloride. The silver halide that precipitates is filtered off and the filtrate concentrated to yield diphenyliodonium fluoroborate which may be purified by recrystallization.

The aromatic iodonium simple salts may be prepared in accordance with Beringer et al., above, by various methods including (1) coupling of two aromatic compounds with iodyl sulfate in sulfuric acid, (2) coupling of two aromatic compounds with an iodate in acetic acid-acetic anhydride-sulfuric acid, (3) coupling of two aromatic compounds with an iodine acrylate in the presence of an acid, and (4) condensation of an iodoso compound, an iodoso diacetate, or an iodoxy compound with another aromatic compound in the presence of an acid. Diphenyliodonium bisulfate is prepared by method (3), for example, by the addition over a period of eight hours at below 5°C of a mixture of 35 ml of conc. sulfuric acid and 50 ml of acetic anhydride to a well-stirred mixture of 55.5 ml of benzene, 50 ml of acetic anhydride, and 53.5g of potassium iodate. The mixture is stirred for an additional four hours at 0°-5°C and at room temperature (about 25°C) for 48 hours and treated with 300 ml of diethyl ether. On concentration, crude diphenyliodonium bisulfate precipitates and may be purified by recrystallization if desired.

The second component in the photoinitiator system is the sensitizer. The sensitizer should be soluble in the photopolymerizable composition, free of functionalities that would substantially interfere with the cationic curing process, and capable of light absorption within the range of wavelengths between about 300 and about 1000 nanometers.

Suitable sensitizers include compounds in the following categories: ketones, coumarin dyes (e.g., ketocoumarins), xanthene dyes, acridine dyes, thiazole dyes, thiazine dyes, oxazine dyes, azine dyes, aminoketone dyes, porphyrins, aromatic polycyclic hydrocarbons, p-substituted aminostyryl ketone compounds, aminotriaryl methanes, merocyanines, squarylium dyes and pyridinium dyes. Ketones (e.g., monoketones or alpha-diketones), ketocoumarins,

aminoarylketones and p-substituted aminostyryl ketone compounds are preferred sensitizers. For applications requiring deep cure (e.g., cure of highly-filled composites), it is preferred to employ sensitizers having an extinction coefficient below about $1000 \text{ l mole}^{-1} \text{ cm}^{-1}$, more preferably about or below $100 \text{ l mole}^{-1} \text{ cm}^{-1}$, at the desired wavelength of irradiation for photopolymerization. The alpha-diketones are an example of a class of sensitizers having this property, and are particularly preferred for dental applications.

By way of example, a preferred class of ketone sensitizers has the formula:



where X is CO or CR^1R^2 where R^1 and R^2 can be the same different, and can be hydrogen, alkyl, alkaryl or aralkyl, b is zero, and A and B can be the same or different and can be substituted (having one or more non-interfering substituents) or unsubstituted aryl, alkyl, alkaryl, or aralkyl groups, or together A and B can form a cyclic structure which can be a substituted or unsubstituted cycloaliphatic, aromatic, heteroaromatic or fused aromatic ring.

Suitable ketones of the above formula include monoketones ($b=0$) such as 2,2-, 4,4- or 2,4-dihydroxybenzophenone, di-2-pyridyl ketone, di-2-furanyl ketone, di-2-thiophenyl ketone, benzoin, fluorenone, chalcone, Michler's ketone, 2-fluoro-9-fluorenone, 2-chlorothioxanthone, acetophenone, benzophenone, 1- or 2-acetonaphthone, 9-acetylanthracene, 2-, 3- or 9-acetylphenanthrene, 4-acetylbiphenyl, propiophenone, n-butyrophenone, valerophenone, 2-, 3- or 4-acetylpyridine, 3-acetylcoumarin and the like. Suitable diketones include aralkyldiketones such as anthraquinone, phenanthrenequinone, o-, m- and p-diacetylbenzene, 1,3-, 1,4-, 1,5-, 1,6-, 1,7- and 1,8-diacetylnaphthalene, 1,5-, 1,8- and 9,10-diacetylanthracene, and the like. Suitable I-diketones ($b=1$ and $\text{X}=\text{CO}$) include 2,3-butanedione, 2,3-pentanedione, 2,3-hexanedione, 3,4-hexanedione, 2,3-heptanedione, 3,4-heptanedione, 2,3-octanedione, 4,5-octanedione, benzil, 2,2'-3,3'- and 4,4'-dihydroxybenzil, furil, di-3,3'-indolyethanedione, 2,3-bornanedione (camphorquinone), biacetyl, 1,2-cyclohexanedione, 1,2-naphthaquinone, acenaphthaquinone, and the like.

Examples of particularly preferred visible light sensitizers include camphorquinone; glyoxal; biacetyl; 3,3,6,6-tetramethylcyclohexanedione; 3,3,7,7-tetramethyl-1,2-cycloheptanedione; 3,3,8,8-tetramethyl-1,2-cyclooctanedione; 3,3,18,18-tetramethyl-1,2-cyclooctadecanedione; dipivaloyl; benzil; furil; hydroxybenzil; 2,3-butanedione; 2,3-pentanedione; 2,3-hexanedione; 3,4-hexanedione; 2,3-heptanedione; 3,4-heptanedione; 2,3-octanedione; 4,5-octanedione; and 1,2-cyclohexanedione. Of these, camphorquinone is the most highly preferred sensitizer.

The third component of the initiator system is an electron donor. The electron donor compound(s) should meet the requirements set forth below and be soluble in the polymerizable composition. The donor can also be selected in consideration of other factors, such as shelf stability and the nature of the polymerizable materials, iodonium salt and sensitizer chosen. A class of donor compounds that may be useful in the inventive systems may be selected from some of the donors described in Palazzotto et al., U.S. Patent No. 5,545,676. Possible donor compounds that meet the criteria set forth by Palazzotto et al. must then be tested using one or both of the methods set forth below to determine if they will be useful donors for the photopolymerizable compositions of the invention.

The donor is typically an alkyl aromatic polyether or an alkyl, aryl amino compound wherein the aryl group is substituted by one or more electron withdrawing groups. Examples of suitable electron withdrawing groups include carboxylic acid, carboxylic acid ester, ketone, aldehyde, sulfonic acid, sulfonate and nitrile groups.

The suitability of a compound for use as an electron donor in the compositions of the invention may be determined by measuring the photoinduced potential of a sample photoinitiator system that includes the compound. The photoinduced potential can be evaluated in the following manner. A standard solution is prepared that contains 2.9×10^{-5} moles/g of diphenyl iodonium hexafluoroantimonate and 1.5×10^{-5} moles/g of camphorquinone in 2-butanone. A pH electrode is then immersed in the solution and a pH meter is calibrated to zero mV. A test solution of the standard solution and the compound is prepared next

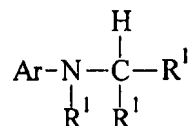
using the compound at a concentration of 2.9×10^{-5} moles/g. This test solution is irradiated using blue light having a wavelength of about 400 to 500 nm having an intensity of about 200 to 400 mW/cm² for about 5 to 10 seconds at a distance of about 1 mm. Millivolts relative to the standard solution are then determined by
5 immersing the pH electrode in the test solution and obtaining a mV reading on the pH meter. Useful donors are those compounds that provide a reading of at least 100mV relative to the standard solution, and preferably provide a gel time for the compositions that is at least about 30 to 40 percent shorter than for compositions that do not contain the donor. Higher mV readings are generally indicative of
10 greater activity.

In some instances there may be some uncertainty regarding the outcome of the above procedure. This may be due to questions or uncertainty arising from the instrumentation employed, from the way the procedure was carried out, or other factors, or one may wish to verify the suitability of a particular
15 compound. A second test may be performed to verify the result obtained by following the above procedure and resolve any such uncertainty.

The second method involves the evaluation of the photoinduced potential of an initiator system that includes the compound compared to a system that includes 3-dimethylamino benzoic acid. For this method, a standard solution
20 of 2.9×10^{-5} moles/g diphenyl iodonium hexafluoroantimonate, 1.5×10^{-5} moles/g camphorquinone and 2.9×10^{-5} moles/g of 3-dimethylaminobenzoic acid in 2-butanone is prepared. A pH electrode is then immersed in the solution and a pH meter is calibrated to zero mV. The standard solution is irradiated with blue light having a wavelength of between about 400-500 nm and an intensity of about 200 to
25 400 mW/cm² for about 5 to 10 seconds using a focused light source such as a dental curing light at a distance of about 1 mm. After light exposure, the potential of the solution is measured by immersing a pH electrode in the irradiated standard solution and reading the potential in mV using a pH meter. A test solution is then prepared using 2.9×10^{-5} moles/g of diphenyl iodonium hexafluoroantimonate,
30 1.5×10^{-5} moles/g of camphorquinone and 2.9×10^{-5} moles/g of the compound in 2-butanone. The test solution is irradiated and the photoinduced potential measured

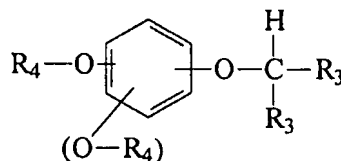
using the same technique as described for the standard solution. If the test solution has a photoinduced potential that is the same as or greater than that of the 3-dimethylaminobenzoic acid containing standard solution, then the compound is a useful donor.

- 5 A preferred group of alkyl, aryl amine donor compounds is described by the following structural formula:



- wherein R^1 are independently H, C_{1-18} alkyl that is optionally substituted by one or more halogen, -CN, -OH, -SH, C_{1-18} alkoxy, C_{1-18} alkylthio, C_{3-18} cycloalkyl, aryl,
 10 COOH , COOC_{1-18} alkyl, $(\text{C}_{1-18} \text{ alkyl})_{0-1}-\text{CO}-\text{C}_{1-18}$ alkyl, SO_3R^2 , CN or or aryl that is optionally substituted by one or more electron withdrawing groups or the R^1 groups may be joined to form a ring; and Ar is aryl that is substituted by one or more electron withdrawing groups. Suitable electron withdrawing groups include -
 COOH , $-\text{COOR}^2$, $-\text{SO}_3\text{R}^2$, -CN, $-\text{CO}-\text{C}_{1-18}$ alkyl and $-\text{C}(\text{O})\text{H}$ groups.

- 15 A preferred group of aryl alkyl polyethers has the following structural formula:



- wherein $n = 1-3$ each R_3 is independently H or C_{1-18} alkyl that is optionally
 20 substituted by one or more halogen, -CN, -OH, -SH, C_{1-18} alkoxy, C_{1-18} alkylthio, C_{3-18} cycloalkyl, aryl, substituted aryl, $-\text{COOH}$, $-\text{COOC}_{1-18}$ alkyl, $-(\text{C}_{1-18} \text{ alkyl})_{0-1}-\text{COH}$, $-(\text{C}_{1-18} \text{ alkyl})_{0-1}-\text{CO}-\text{C}_{1-18}$ alkyl, $-\text{CO}-\text{C}_{1-18}$ alkyl, $-\text{C}(\text{O})\text{H}$ or $-\text{C}_{2-18}$ alkenyl groups and each R_4 can be C_{1-18} alkyl that is optionally substituted by one or more
 25 halogen, -CN, -OH, -SH, C_{1-18} alkoxy, C_{1-18} alkylthio, C_{3-18} cycloalkyl, aryl, substituted aryl, $-\text{COOH}$, $-\text{COOC}_{1-18}$ alkyl, $-(\text{C}_{1-18} \text{ alkyl})_{0-1}-\text{COH}$, $-(\text{C}_{1-18} \text{ alkyl})_{0-1}-\text{CO}-\text{C}_{1-18}$ alkyl, $-\text{CO}-\text{C}_{1-18}$ alkyl, $-\text{C}(\text{O})\text{H}$ or $-\text{C}_{2-18}$ alkenyl groups.

In each of the above formulas the alkyl groups can be straight-chain or branched, and the cycloalkyl group preferably has 3 to 6 ring carbon atoms but may have additional alkyl substitution up to the specified number of carbon atoms. The aryl groups may be carbocyclic or heterocyclic aryl, but are preferably carbocyclic and more preferably phenyl rings.

Preferred donor compounds include 4-dimethylaminobenzoic acid, ethyl 4-dimethylaminobenzoate, 3-dimethylaminobenzoic acid, 4-dimethylaminobenzoin, 4-dimethylaminobenzaldehyde, 4-dimethylaminobenzonitrile and 1,2,4-trimethoxybenzene.

The photoinitiator compounds are provided in an amount effective to initiate or enhance the rate of cure of the resin system. It has been found that the amount of donor that is used can be critical particularly when the donor is an amine. Too much donor can be deleterious to cure properties. Preferably, the sensitizer is present in about 0.05-5 weight percent based on resin compounds of the overall composition. More preferably, the sensitizer is present at 0.10-1.0 weight percent. Similarly, the iodonium initiator is preferably present at 0.05-10.0 weight percent, more preferably at 0.10-5.0 weight percent, and most preferably 0.50-3.0 weight percent. Likewise, the donor is preferably present at 0.01-5.0 weight percent, more preferably 0.05-1.0 weight percent, and most preferably 0.05-0.50 weight percent.

The photopolymerizable compositions of the invention are prepared by simply admixing, under "safe light" conditions, the components of the inventive compositions. Suitable inert solvents may be employed if desired when effecting this mixture. Any solvent may be used which does not react appreciably with the components of the inventive compositions. Examples of suitable solvents include acetone, dichloromethane, and acetonitrile. A liquid material to be polymerized may be used as a solvent for another liquid or solid material to be polymerized. Solventless compositions can be prepared by simply dissolving the aromatic iodonium complex salt and sensitizer in the epoxy resin polyol mixture with or without the use of mild heating to facilitate dissolution.

The compositions of the present invention provide a very useful combination of cure speed, cure depth and shelf life. They cure well even when loaded with large amounts of fillers, and can be used in a variety of applications including graphic arts imaging (e.g. for color proofing systems, curable inks, or silverless imaging), printing plates (e.g. projection plates or laser plates), photoresists, solder masks, electronic conformal coatings, coated abrasives, magnetic media, photocurable adhesives (e.g. for orthodontics) and photocurable composites (e.g., for autobody repair or dentistry).

Dental applications particularly benefit from the unique compositions of the present invention. Until now, acrylate and methacrylate chemistry has been used extensively for adhesive and restorative dental compositions. This chemistry has the advantage of being curable with visible light using photoinitiator systems, but has the disadvantage of undergoing a relatively high degree of shrinkage during the polymerization process. In contrast, during polymerization the epoxy resins found in the compositions of the present invention shrink significantly less than the acrylate and methacrylate resins of the prior art. The present invention provides a system for curing epoxy/polyol resin systems, with or without the presence of an acrylate or methacrylate in an acceptable time frame and to a sufficient depth using visible light source equipment already available in the dental office.

The dental materials may be filled or unfilled and include dental materials such as direct esthetic restorative materials (e.g., anterior and posterior restoratives), prostheses, adhesives and primers for oral hard tissues, sealants, veneers, cavity liners, orthodontic bracket adhesives for use with any type of bracket (such as metal, plastic and ceramic), crown and bridge cements, artificial crowns, artificial teeth, dentures, and the like. These dental materials are used in the mouth and are disposed adjacent to natural teeth. The phrase "disposed adjacent to" as used herein refers to the placing of a dental material in temporary or permanent bonding (e.g., adhesive) or touching (e.g., occlusal or proximal) contact with a natural tooth. The term "composite" as used herein refers to a filled dental material. The term "restorative" as used herein refers to a composite which is

polymerized after it is disposed adjacent to a tooth. The term "prosthesis" as used herein refers to a composite which is shaped and polymerized for its final use (e.g., as crown, bridge, veneer, inlay, onlay or the like) before it is disposed adjacent to a tooth. The term "sealant" as used herein refers to a lightly filled composite or to an unfilled dental material which is cured after it is disposed adjacent to a tooth. "Polymerizable" refers to curing or hardening the dental material, e.g., by free-radical, cationic or mixed reaction mechanisms.

In certain applications, the use of a filler may be appropriate. The choice of filler affects important properties of the composite such as its appearance, radiopacity and physical and mechanical properties. Appearance is affected in part by adjustment of the amounts and relative refractive indices of the ingredients of the composite, thereby allowing alteration of the translucence, opacity or pearlescence of the composite. Epoxy resin compositions of the invention, either alone or in admixture with diluent monomer, can be prepared with refractive indices which approach or approximate the refractive indices of fillers such as quartz (refractive index 1.55), submicron silica (refractive index 1.46), and 5.5:1 mole ratio SiO:ZrO, non-vitreous microparticles (refractive index 1.54). In this way the appearance of the dental material can, if desired, be made to closely approximate the appearance of natural dentition.

Radiopacity is a measurement of the ability of the composite to be detected by x-ray examination. Frequently a radiopaque composite will be desirable, for instance, to enable the dentist to determine whether or not a dental restoration remains sound. Under other circumstances a non-radiopaque composite may be desirable.

The amount of filler which is incorporated into the composite, referred to herein as the "loading level" and expressed as a weight percent based on the total weight of the dental material, will vary depending on the type of filler, the epoxy resin and other components of the composition, and the end use of the composite.

For some dental materials, such as sealants, the epoxy resin compositions of the invention can be lightly filled (e.g., having a loading level of

less than about 40 weight percent) or unfilled. Preferably the viscosity of the dental material is sufficiently low to allow its penetration into pits and fissures of occlusal tooth surfaces as well as into etched areas of enamel, thereby aiding in the retention of the dental material. In applications where high strength or durability are desired (e.g., anterior or posterior restoratives, prostheses, crown and bridge cements, artificial crowns, artificial teeth and dentures) the loading level can be as high as about 95 weight percent. For most dental restorative and prosthetic applications a loading level of between about 70 and 90 weight percent is generally preferred.

Fillers may be selected from one or more of any material(s) suitable for incorporation in compositions used for medical applications, such as fillers currently used in dental restorative compositions and the like. The filler is finely divided and preferably has a maximum particle diameter of less than about 50 micrometers and an average particle diameter of less than about 10 micrometers.

The filler can have a unimodal or polymodal (e.g., bimodal) particle size distribution. The filler can be an inorganic material. It can also be a crosslinked organic material that is insoluble in the polymerizable resin, and is optionally filled with inorganic filler. The filler should in any event be non-toxic and suitable for use in the mouth. The filler can be radiopaque, radiolucent or nonradiopaque.

Examples of suitable inorganic fillers are naturally-occurring or synthetic materials such as quartz, nitrides (e.g., silicon nitride), glasses derived from, for example Ce, Sb, Sn, Zr, Sr, Ba and Al, colloidal silica, feldspar, borosilicate glass, kaolin, talc, titania, and zinc glass; low Mohs hardness fillers such as those described in U.S. Patent No. 4,695,251; and submicron silica particles (e.g., pyrogenic silicas such as the "Aerosil" Series "OX 50", "130", "150" and "200" silicas sold by Degussa and "Cab-O-Sil M5" silica sold by Cabot Corp.). Examples of suitable organic filler particles include filled or unfilled pulverized polycarbonates, polyepoxides, and the like. Preferred filler particles are quartz, submicron silica, and non-vitreous microparticles of the type described in U.S. Patent No. 4,503,169. Metallic fillers may also be incorporated, such as particulate metal filler made from a pure metal such as those of Groups IVA, VA,

VIA, VIIA, VIII, IB, or IIB, aluminum, indium, and thallium of Group IIIB, and tin and lead of Group IVB, or alloys thereof. Conventional dental amalgam alloy powders, typically mixtures of silver, tin, copper, and zinc, may also optionally be incorporated. The particulate metallic filler preferably has an average particle size of about 1 micron to about 100 microns, more preferably 1 micron to about 50 microns. Mixtures of these fillers are also contemplated, as well as combination fillers made from organic and inorganic materials. Fluoroaluminosilicate glass fillers, either untreated or silanol treated, are particularly preferred. These glass fillers have the added benefit of releasing fluoride at the site of dental work when placed in the oral environment.

Optionally, the surface of the filler particles may be treated with a surface treatment such as a coupling agent in order to enhance the bond between the filler and the polymerizable resin. The coupling agent may be functionalized with reactive curing groups, such as acrylates, methacrylates, epoxies, and the like. Examples of coupling agents include silanes such as gamma-methacryloxypropyltrimethoxysilane, gamma-mercaptopropyltriethoxysilane, beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, gamma-glycidoxypropyltrimethoxysilane, and the like.

The materials of the present invention can also contain suitable adjuvants such as accelerators, inhibitors, absorbers, stabilizers, pigments, dyes, viscosity modifiers, surface tension depressants and wetting aids, antioxidants, and other ingredients well known to those skilled in the art.

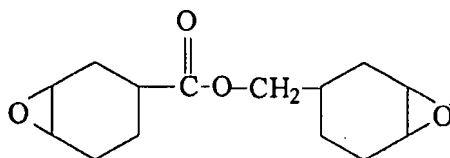
The amounts and types of each ingredient in the dental material should be adjusted to provide the desired physical and handling properties before and after cure. For example, the cure rate, cure stability, fluidity, compressive strength, tensile strength and durability of the dental material typically are adjusted in part by altering the types and amounts of polymerization initiator(s) and, if present, the loading and particle size distribution of filler(s). Such adjustments typically are carried out empirically based on experience with dental materials of the prior art.

When the dental material is applied to a tooth, the tooth can optionally be pre-treated with a primer such as dentin or enamel adhesive by methods known to those skilled in the art.

The invention is further described by reference to the following examples, which are understood to be merely illustrative and not limiting the invention in any way.

Example 1

A stock resin solution ("SL1") of an epoxy resin and polyol containing material was prepared by combining 0.50 g camphorquinone, 1.50 g diphenyliodoniumhexafluoroantimonate (DPI SbF₆) with 24.50g UVR 6105 cycloaliphatic diepoxide and 0.50g of polytetrahydrofuran diol having an average molecular weight of 250 (pTHF-250) and stirring until homogeneous in the absence of light. UVR 6105 is a cycloaliphatic diepoxide having the following formula:



A variety of donor compounds were evaluated for their photoinduced potential and ability to enhance cure speed. To evaluate the photoinduced potential of the compounds, a stock initiator solution was prepared by transferring 0.50 grams camphorquinone and 3.00 grams of DPI SbF₆ to a 250 ml polyethylene screw-top bottle. Two hundred grams of 99.5+% 2-butanone was transferred to the polyethylene bottle and the contents mixed until homogeneous. The resulting solution contained approximately 2.9×10^{-5} moles DPISbF₆/gram and 1.5×10^{-5} moles CPQ/gram. The electron donor additives were evaluated at a concentration of 2.9×10^{-5} moles donor/gram of SL1. Samples were prepared by transferring 1.16×10^{-4} moles of donor to a 13 ml glass vial followed by the addition of 4.0 grams of the stock initiator solution. Vials were capped and

vigorously shaken until homogeneous. Samples were then evaluated for relative potential according to the following procedure:

A semi-micro combination pH electrode (Corning model 476540) was connected to a pH meter with millivolt capability (Beckman Φ P/N 123133).

5 The stock initiator solution was used as the millivolt standard in this evaluation. Four grams of the stock initiator solution were transferred to a 13 ml glass vial along with a micro-magnetic stir bar. The sample was placed above a magnetic stirrer which initiated slow stirring of the sample. The electrode was rinsed with water followed by ethanol and then thoroughly dried with a paper towel. The
10 electrode was immersed in the stock initiator solution and the millivolt reading calibrated to read 0.00 mV. The electrode was removed and the sample was irradiated with a Visilux dental curing light having an intensity of about 200 mW/cm² at a wavelength of 400 to 500 nm for 10 seconds by placing the tip of the light guide directly flush with the center bottom of the vial. Following irradiation
15 the sample was capped and mixed thoroughly by shaking for about 5 seconds. The electrode was rinsed, cleaned thoroughly with ethanol, blotted dry and immersed in the irradiated solution. The millivolts relative to the control was established by pressing the mV button on the pH meter until a stable reading was obtained. The above procedure was repeated with the various donor solutions. The electrode was
20 calibrated with unirradiated stock initiator solution before each run as described previously.

The donor compounds were also evaluated for their effect on cure speed of the stock resin solution. Approximately one gram samples were prepared by transferring 2.9×10^{-5} moles of each prospective donor to 1 dram glass vials
25 followed by 1.0 grams of the stock resin solution. The ingredients were mixed until homogeneous. Each sample was examined for gel time by transferring the solution to a 6 mm diameter and 2.5 mm thick Teflon mold with a polyester film clamped in direct contact with the bottom face. The sample was placed directly beneath the light guide of a Visilux 2 dental curing light at a distance of 10 mm.
30 Samples were irradiated and probed to establish hard gel times up to a maximum of 60 seconds. Results are reported in Table 1. Throughout the examples, "NC"

means that the material did not cure and "NT" means that the material was not tested.

TABLE I

Sample #	Donor Compound	gms donor/gm resin	gel time (sec)	mv (initial) MEK	mv (photo) MEK
1	none	none	25	0	-25
2	4-dimethylaminobenzoic acid	0.0047	7	-11	184
3	ethyl 4-dimethylaminobenzoate	0.0053	7	-12	200
4	3-dimethylaminobenzoic acid	0.0047	12	-5	115
5	1,2,4-trimethoxybenzene	0.0053	7	-3	233
6	4-dimethylaminobenzoin	0.0068	9	-13.4	261
7	4-dimethylaminobenzonitrile	0.0045	16 (top)	9.7	266
8	4-dimethylaminobenzaldehyde	0.0043	16 (top)	8	245
9	4-dimethylaminophenethanol	0.0046	NC	-83.2	17
10	dimethylaniline	0.0043	20	-55	54
11	2,5-dimethoxybenzylalcohol	0.0049	25	30.8	52
12	tetrahydrofurfuralalcohol	0.0030	25	-34	-10
13	1,2,3-trimethoxybenzene	0.0050	25	-1.9	5
14	1,3,5-trimethoxybenzene	0.0050	24	10.1	28
15	benzyl alcohol	0.0031	26	-13.7	24
16	2,4,6-pentamethylaniline	0.0050	22	10	71.3
17	N,N-dimethylbenzylamine	0.0040	25	-189.7	-170
18	triethanolamine	0.0042	NC	-171	-162
19	dihydroxyethyl-p-toluidine	0.0058	NC	-180	-98
20	4-t-butyl N,N-dimethylaniline	0.0050	34	NT	NT

Example 2

A stock solution of an epoxy resin/polyol/acrylate resin material was prepared by transferring 0.50g camphorquinone and 1.50g DPI SbF₆ to a glass jar followed by the addition of approximately 0.20g of dichloromethane solvent,
5 70.56g of UVR 6105, 9.80g of Ebecryl 1830 polyester hexacrylate (Radcure Specialties) and 17.64g of pTHF-250. The mixture was stirred until homogeneous in the absence of light.

Three donor compounds were evaluated for photoinduced potential and for their ability to enhance the cure speed of the epoxy/polyol/acrylate resin
10 material.

To evaluate the photoinduced potential of the compounds, a stock initiator solution ("SL2") was prepared by transferring 0.50 grams camphorquinone and 3.00 grams of DPI SbF₆ to a 250 ml polyethylene screw-top bottle. Two hundred grams of 99.5+% 2-butanone were transferred to the
15 polyethylene bottle and the contents mixed until homogeneous. The resulting solution contained approximately 2.9×10^{-5} moles DPISbF₆/gram and 1.5×10^{-5} moles CPQ/gram. The electron donor additives were evaluated at a concentration of 2.9×10^{-5} moles donor/gram of SL2. Samples were prepared by transferring 1.16×10^{-4} moles of donor to a 13 ml glass vial followed by the addition of 4.0
20 grams of the stock initiator solution. Vials were capped and vigorously shaken until homogeneous. Samples were then evaluated for relative potential according to the procedure detailed in Example 1.

The donor compounds were evaluated for their effect on cure speed of the epoxy/polyol/acrylate resin solution. Approximately one gram samples were
25 prepared by transferring 2.9×10^{-5} moles of each prospective donor to 1 dram glass vials followed by 1 drop of dichloromethane solvent and 1.0 grams of the stock resin material. The ingredients were mixed until homogeneous. Each sample was examined for gel time by transferring the solution to a 6 mm diameter and 2.5 mm thick Teflon mold with a polyester film clamped in direct contact with the bottom
30 face. The sample was placed directly beneath the light guide of a Visilux 2 dental curing light at a distance of 3 cm. Samples were irradiated up to a maximum of

120 seconds and probed to establish soft and hard gel times. Results are reported in Table 2.

TABLE 2

Donor Compound	gms donor/ gm resin	gel time (sec)	Mv (initial)	Mv (photo)
none	none	120	0	-25
4-dimethylaminobenzoic acid	0.0047	30	-11	184
ethyl 4-dimethylaminobenzoate	0.0053	35	-12	200
4-dimethylaminobenzoin	0.0068	70	-13	261

5 **Example 3**

A bifunctional epoxy/acrylate material was prepared according to the following procedure:

10 Epon 828 Bis Phenol-A-diepoxide (82.9 grams, 0.22 moles) was transferred to 250 ml three-necked resin flask which was fitted with a condenser, an air driven stir rod with a Teflon stir blade and an addition funnel. The system was kept dry with a calcium sulfate drying tube. The resin reactor was partially immersed in an oil bath heated to about 100°C and the diepoxide allowed to equilibrate to this temperature for about 30 minutes. Triphenyl antimony (1.1 grams) was transferred to the diepoxide and allowed to dissolve for about 15 minutes. Methacrylic acid (17.2 grams, 0.20 moles) was weighed into the addition funnel and then slowly added to the heated diepoxide slowly over about 3 hours. The mixture was allowed to react for a total of 24 hours yielding a high viscosity liquid which comprised a statistical mixture of monoepoxide/monomethacrylate adduct and both diepoxide and dimethacrylate.

20

Example 4

Two epoxy/acrylate polyol compositions were prepared from the reaction product of example 3 as shown below with and without diphenyliodonium salt (DPISbF₆):

Ingredient	Sample 1	Sample 2
	Parts by Weight	Parts by Weight
UVR6105 epoxy	64.00	64.00
Product of Example 2	20.00	20.00
pTHF-250	16.60	16.60
DPISbF ₆	0.00	1.50
CPQ	0.50	0.50
EDMAB	0.56	0.56

Samples approximately 2.5 mm thick were irradiated with a Visilux 2 Dental curing light from a distance of about 10 mm for about 30 seconds. Both samples were relatively soft and flexible and failed to register a BarCol hardness value. Samples were transferred to an oven at 37°C for 24 hours. Sample 1 remained relatively soft whereas Sample 2 with DPISbF₆ was a hard solid with a barcol hardness value of about 30. The data shows that the initial gelation is attributed to the free radical polymerization from the reaction product of example 3 and subsequent polymerization results from cationic curing of the epoxy resin UVR 6105 and reaction product of example 3, and that addition of the diphenyl iodonium salt or compound provides cationic curing in addition to free radical curing.

15 **Example 5**

The effect of various diphenyl iodonium salts was evaluated in epoxy resin/polyol compositions with and without the presence of an aromatic amine. Three epoxy/polyol containing compositions were prepared as follows:

Composition A(1)

Parts by Weight

UVR 6105	80.0
pTHF-250	20.0
Camphorquinone	0.50
DPI SbF ₆	1.50

Composition B(1)

UVR 6105	80.0
pTHF-250	20.0
Camphorquinone	0.50
DPI PF ₆	1.23

5 Composition C(1)

UVR 6105	80.0
pTHF	20.0
Camphorquinone	0.50
DPI C1	0.90

Ethyl 4-dimethylaminobenzoate (EDMAB) was added to a portion of the above compositions in an amount of 0.56 parts by weight per 100 parts of each of A(1), B(1) and C(1), forming compositions A(2), B(2) and C(2) respectively.

Each composition was prepared by combining the ingredients at room temperature and stirring until homogeneous. Each composition was evaluated for cure speed by irradiation of a 2 mm thick sample with light at a wavelength of 400-500 nm from a Visilux 2 light source at a distance of 10 mm. Irradiation continued for 120s or until a soft or hard gel was formed. Results are reported in Table 3.

Table 3

Composition	Gel time (seconds)
A(1)	14
B(1)	16
C(1)	NC
A(2)	8
B(2)	8
C(2)	NC

This data illustrates that enhanced cure speed can be achieved when the amine electron donor EDMAB is used in combination with an iodonium salt with a PF_6 or SbF_6 counterion. No curing was observed when Cl was the counterion, with or without the donor EDMAB.

Example 6

A variety of visible light absorbing sensitizers were evaluated in epoxy/polyol formulations containing 1.50% Ph_2ISbF_6 , 0.50% sensitizer compound and optionally 0.56% EDMAB by weight. Solutions A and B, without and with EDMAB respectively were prepared as shown below:

	Solution A	Solution B
Ingredient	Parts by Weight	Parts by Weight
UVR6105	80.00	80.00
pTHF-250	20.00	20.00
DPISbF ₆	1.50	1.50
EDMAB	---	0.56

Sensitizers were evaluated by transferring 0.0050 grams of the sensitizer to a 2 dram glass vial followed by the addition of 2 drops of dichloromethane solvent and 1.0 grams of solution A. Compositions were mixed until homogeneous and evaluated for gel time as described in example 1. The

same procedure was repeated for solution B. Set out in Table 4 are the run numbers, sensitizer and the gel times with and without EDMAB.

Table 4			
Sample #	Sensitizer Compound	Gel time/no EDMAB	Gel time/EDMAB
	(0.0050 gm/gm resin)	(seconds)	(seconds)
1	None	NC	NC
2	Camphorquinone	14	8
3	2-Chlorothioxanthone	25 (surface only)	15
4	Fluorenone	NC	30 (top 1 mm)
5	Furil	115	40
6	Dibromofluorescein	70	17
7	Fluorescein	95 (surface only)	91 (surface only)
8	Ethyl Eosin	64 (surface only)	15
9	Eosin y	19 (surface only)	20 (complete cure)
10	Benzoylbenzocoumarin	NC	15
11	Rose Bengal	NC	26
12	Isopropylthioxanthone	11 (surface only)	20 (complete cure)
15	Anthraquinone	30 (surface only)	90 (complete cure)
16	Diethoxyanthracene	20 (surface only)	40 (surface only)
17	2-ethyl-9,10 dimethoxyanthracene	22 (surface only)	45 (surface only)
18	9,10 dichloroanthracene	NC	NC
19	Diphenyl isobenzofuran	32	41
20	Methylene violet	NC	NC

- 5 The data illustrates that a variety of ketone functional sensitizers in combination with DPISbF₆ and the electron donor EDMAB photocures faster and/or more completely than those formulations with sensitizer and DPISbF₆ alone.

Example 7

The effect of EDMAB to DPISbF₆ molar ratio on gel time was examined. Molar ratios of EDMAB/ DPISbF₆ ranging from 0 to 8.0 were investigated. Solution A was prepared by combining 16.0g UVR 6105, 4.0g pTHF-250, 0.10g camphorquinone and 0.30g DPISbF₆. This solution contained 2.9x10⁻⁵ moles of DPISbF₆ per gram of resin. Solution B was prepared by transferring 0.44 grams of EDMAB to a glass vial followed by 10.0 grams of solution A resulting in a formulation containing 2.3x10⁻⁴ moles of EDMAB per gram of resin or 8 molar equivalents of EDMAB/ DPISbF₆. 1 gram mixtures of Solutions A and B were prepared and evaluated for gel time as described in Example 1, however the irradiation distance was 10 mm. Set out in Table 5 are the run numbers, grams of solutions A and B, the molar ratio of amine to onium salt and the gel times.

The data illustrates that significant cure speed enhancement can be achieved with as little as 0.08 equivalents of EDMAB relative to onium salt. Optimal cure speed is achieved with approximately 0.10 to 1.0 equivalents. Further addition of EDMAB beyond 1.0 equivalents results in a near linear increase in gel time (inhibition) and decrease in material hardness.

Table 5					
Sample #	Grams solution B	Grams solution A	Molar Ratio EDMAB/ Onium	Gel time	Comments
	2.32x10 ⁻⁴ moles EDMAB/gm	2.0x10 ⁻⁵ moles onium/gm		(seconds)	
1	0.00	1.00	0.00	18	hard solid
2	0.01	0.99	0.08	9	hard solid
3	0.02	0.98	0.16	7	hard solid
4	0.03	0.97	0.25	8	hard solid
5	0.05	0.95	0.40	8	hard solid

Table 5					
Sample #	Grams solution B	Grams solution A	Molar Ratio EDMAB/ Onium	Gel time	Comments
	2.32×10^{-4} moles EDMAB/gm	2.0×10^{-5} moles onium/gm		(seconds)	
6	0.10	0.90	0.80	8	hard solid
7	0.20	0.80	1.60	13	hard solid
8	0.30	0.70	2.40	15	hard gel
9	0.40	0.60	3.20	20	hard gel
10	0.50	0.50	4.00	21	hard gel
11	0.60	0.40	4.80	25	soft gel
12	0.70	0.30	5.60	30	soft gel
13	0.80	0.20	6.40	35	soft gel
14	0.90	0.10	7.20	55	soft gel
15	1.00	0.00	8.00	60	soft gel

The data shows that the addition of the amine donor EDMAB can both enhance and decrease the cure speed and properties based on low and high concentrations, respectively, relative to the absence of EDMAB

5

Example 8

Eighteen photocurable epoxy/polyol resin formulations were prepared with the component concentrations as shown in Table 5 for a $2^{(5-1)}$ fractional factorial design experiment. The five experimental variables in the study were:

10

- A) % camphorquinone (CPQ),
- B) % diphenyliodonium hexafluoroantimonate (DPISbF6),
- C) % ethyl-4-dimethyl aminobenzoate (EDMAB),

- D) ratio of aliphatic to cycloaliphatic diepoxides (EPON/UVR ratio),
- E) % polytetrahydrofuran MW 250 (pTHF).

The aliphatic diepoxide used was diglycidyl ether of bisphenol A (Epon 828, Shell Oil Co.); the cycloaliphatic diepoxide used was 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (UVR-6105).

Gel time of each of the prepared resin solutions was tested under continuously irradiating of a Visilux-2 dental curing light. Three millimeter thick cylindrical Teflon BarCol Hardness molds were filled with uncured resin. The uncured resin in each mold was then irradiated at a distance of 1 cm with a Visilux-2 dental curing light while being frequently probed with a plastic mixing stick. The time in seconds at which the resin began to thicken and exhibit properties of a soft solid was recorded as gel time. The average of three such tests for each resin formulation is tabulated in Table 6 alongside the corresponding compositional information for each resin formulation.

The statistical analysis (YATES ANOVA) indicates that EDMAB was a statistically significant variable with an average effect of 7.7 seconds reduction in gel time when 1 molar equivalent (based on DPISbF6) is added to the resin formulations.

Table 6							
VISIBLE LIGHT CURED EPOXY FORMULATIONS							
WITH DPISbF ₆ IN EPOXY/POLYOL RESIN							
Resin Variables			2(5-1) Fractional Factorial				
		Variable	(-)	0	(+)		
% Camphorquinone		Sensitizer	0.25%	0.50%	0.75		
% DPISbF6 (CD-1012)		Catalyst	0.50%	1.00%	2.00%		
EDMAB (DPISbF6 equiv.)		Electron donor	(0 eq.)	(0.5 eq.)	(1 eq.)		
EPON 828:UVR-6105 Ratio		Epoxy resins	1:2	1:1	2:1		
% Polytetrahydrofuran		Polyol	10%	20%	30%		
		1equiv. EDMAB=Grams DPISbF6(193/516)					
		mol. wt. EDMAB = 193	mol. wt. DPISbF6 = 516				
WEIGHT PERCENT OF COMPONENTS IN ACTIVATED RESIN							
DESIGN ORDER	CPQ	DBISbF6	EDMAB	EPON 828	UVR6105	pTHF (250)	GEL TIME
	(grams)	(grams)	(grams)	(grams)	(grams)	(grams)	(seconds)
1	0.25	0.50	0.00	23.08	46.17	30.00	14.3
2	0.75	0.50	0.00	29.58	59.17	10.00	24.0
3	0.25	2.00	0.00	29.25	58.50	10.00	46.0
4	0.75	2.00	0.00	22.42	44.83	30.00	14.0
5	0.25	0.50	0.19	29.69	59.37	10.00	12.6
6	0.75	0.50	0.19	22.85	45.71	30.00	11.0
7	0.25	2.00	0.75	22.33	44.67	30.00	18.0
8	0.75	2.00	0.75	28.83	57.67	10.00	13.3
9	0.25	0.50	0.00	59.50	29.75	10.00	37.3
10	0.75	0.50	0.00	45.83	22.92	30.00	23.0
11	0.25	2.00	0.00	45.17	22.58	30.00	23.6
12	0.75	2.00	0.00	58.17	29.08	10.00	39.0
13	0.25	0.50	0.19	46.04	23.02	30.00	30.6

Table 6 VISIBLE LIGHT CURED EPOXY FORMULATIONS WITH DPISbF₆ IN EPOXY/POLYOL RESIN							
14	0.75	0.50	0.19	59.04	29.52	10.00	17.6
15	0.25	2.00	0.75	58.00	29.00	10.00	26.6
16	0.75	2.00	0.75	44.33	22.17	30.00	30.0
17	0.50	1.00	0.19	39.15	39.16	20.00	11.3
18	0.50	1.00	0.19	39.16	39.15	20.00	11.3

Response: GEL TIME				
VAR	VARIABLE	UNITS	-1 LEVEL	+1 LEVEL
A	CPQ	%	0.250	0.750
B	DPISbF ₆		-0.301	0.301
C	EDMAB		0.000	1.000
D	828:UVR		0.333	0.666
E	pTHF	%	10.000	30.000

VARIABLE	COEFFICIENT	STANDARDIZED EFFECT	SUM OF SQUARES
OVERALL AVERAGE	22.42		
A	-2.32	-4.64	86.0
B	2.51	5.01	100.5
C	-3.84	-7.69	236.4
D	4.66	9.31	346.9
E	-3.24	-6.49	168.4
AB	0.08	0.16	0.1
AC	0.33	0.66	1.8
AD	1.26	2.51	25.3
AE	1.26	2.51	25.3

VARIABLE	COEFFICIENT	STANDARDIZED EFFECT	SUM OF SQUARES
OVERALL AVERAGE	22.42		
BC	-0.49	-0.99	3.9
BD	-1.17	-2.34	21.9
BE	-1.67	-3.34	44.6
CD	1.58	3.16	40.0
CE	5.68	11.36	516.4
DE	1.58	3.16	40.0
CENTER POINT	-12.51		278.1

Example 9 (Preparative Example)

200.3 grams of deionized water was weighed into a 1000 ml rigid poly beaker and adjusted to a pH of 3.02 with trifluoroacetic acid (Aldrich Chem. Co., Milwaukee, WI). 9.9099 grams of 3-glycidoxypyriltrimethoxysilane (United Chemical Technologies, Inc., Bristol, PA) was slowly added to the water while stirring with a magnetic Teflon coated stirring rod. About 50 ml of denatured ethanol was used to rinse the silane addition beaker, and then added to the hydrolyzing aqueous silane solution. The solution was allowed to stir for about 65 minutes (hydrolysis time) and then 200 grams of a 90/10 weight blend of ball mill ground mined quartz, average particle size 2.25-3.15 microns (3M Co., Maplewood, MN, PMC-41-5300-0422-9) and a commercially available fumed silica, Aerosil OX-50 (Degussa Inc., Frankfurt, GE) was slowly added to the silane treatment solution. The resulting slurry was stirred for 27 hours at room temperature. The slurry was then divided evenly among three 1000 ml poly beakers each beaker placed in a convection drying oven for 12 hours at 60°C. The dried cake from each beaker was recombined, mortar and pestled, and then screen in a sealed container on a shaker through a 74 micron nylon screen. The screened powder was then placed in a one pint jar and dried for a final time for 2 hours at

80°C. After a short cool down the jar was then sealed with a metal cap with foil lined paper seal to reduce the moisture vapor transmission into or out of the jar.

Example 10

5 This example describes the preparation of epoxy/polyol resin-based composite materials containing an iodonium salt, an alpha-diketone and an optional amine electron donor (EDMAB).

Two compositions were prepared as follows:

10

Composition A

	UVR 6105	8.00 g
	pTHF250	2.00 g
	DPI SbF6	0.15 g
15	Camphorquinone (CPQ)	0.05 g
	Total	10.20 g

Composition B

	UVR 6105	8.00 g
20	pTHF250	2.00 g
	DPI SbF6	0.15 g
	CPQ	0.05 g
	EDMAB	0.05 g
	Total	10.20 g

25

Each composition was prepared by combining the ingredients at room temperature and stirring until homogeneous.

Two composite materials were further prepared by combining 7.50 grams of the filler from Example 9 with 2.50 grams of Compositions A and B respectively. Samples were spatulated until a thick homogeneous paste was obtained

30

Composite A

	Composition A	2.50 g
	Filler from Example 9	7.50 g
5	Total	10.00 g

Composite B

	Composition B	2.50 g
	Filler from Example 9	7.50 g
10	Total	10.00 g

Samples were evaluated for photopolymerization by determining the BarCol A hardness of 2 mm thick sample according to the following procedure. A 2 mm thick Teflon block which had a cylindrical hole with a diameter of about 6 mm that extended through the thickness of the block was placed on a film of transparent polyethylene terephthalate (PET) such that one end of the of the open cylindrical hole of the die was covered by the PET film. The Teflon die was filled with the sample and another film of PET placed on top of the die covering paste sample. Hand pressure was applied to the PET film to provide an approximately 2 mm thick sample. samples were irradiated with the Visilux 2 light source for 30 seconds by placing the light wand directly on the PET film which covered the sample at the top of the die. Five sets of samples were prepared in triplicate and stored at for 5 minutes, 20 minutes and 24 hours at 25°C and 20 minutes and 24 hours at 37°C respectively. after storage, the PET films were removed and the BarCol hardness of the top and bottom of the die was measured using a Barber-Coleman Impressor (a hand-held portable hardness tester; Model GYZJ 934-1; from Barber Coleman Company Industrial Instruments Division, Lovas Park, IN) equipped with an indenter. For each sample tested, three readings were taken at the top and bottom of each sample. The readings were averaged for each composition and storage condition. A hardness value of zero indicated limited or no

polymerization. Bottom hardness values significantly less than those of the top indicate limited depth of cure. Results are summarized in Table 7 below:

Table 7

Sample	Side Tested	Barcol Hardness				
		25°C			37°C	
		5min.	20min.	24hours	20min.	24hours
Composite A (no EDMAB)	Top	48	58	67	66	70
	Bottom	18	40	67	62	67
Composite B (EDMAB)	Top	54	54	56	64	56
	Bottom	52	53	63	67	63

5 The data shows that Composite B which contains the donor EDMAB exhibits greater top and bottom hardness when post-cured for 5 minutes at 25°C, compared to Composite A without EDMAB. This illustrates that the co-catalyst EDMAB significantly enhances the rate of curing of the epoxy/polyol composite.

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Example 11

This example describes the preparation of epoxy/polyol/methacrylate resin-based composite materials containing an iodonium salt, an alpha-diketone and an optional amine electron donor.

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Two compositions were prepared as follows:

Composition A

	UVR 6105	7.20 g
	pTHF250	1.80 g
	Ebecryl 1830	1.00 g
5	DPISbF6	0.15 g
	Camphorquinone	0.05 g
	Total	10.20 g

Composition B

10	UVR 6105	7.20 g
	pTHF250	1.80 g
	Ebecryl 1830	1.00 g
	DPISbF6	0.15 g
	Camphorquinone	0.05 g
15	ethyl-p-dimethylaminobenzoate	0.05 g
	Total	10.25 g

Each composition was prepared by combining the ingredients at room temperature and stirring until homogeneous.

20 Two composite materials were further prepared by combining 7.50 grams of the filler from Example 9 with 2.50 grams of Compositions A and B respectively. Samples were spatulated until a thick homogeneous paste was obtained

**25 Composite A
(no EDMAB)**

Composition A	2.50 g
Filler from Example 9	7.50 g
Total	10.00 g

30

**Composite B
(EDMAB)**

	Composition B	2.50 g
	Filler from Example 9	7.50 g
5	Total	10.00 g

Samples were evaluated for photopolymerization by determining the BarCol A hardness of 2 mm thick sample according to the procedure described in Example 9. Results are summarized in Table 8 below.

10

Table 8

Sample	Side Tested	Barcol Hardness				
		25°C			37°C	
		5min.	20min.	24hours	20min.	24hours
Composite A (no EDMAB)	Top	45	39	66	58	70
	Bottom	0	0	58	17	59
Composite B (EDMAB)	Top	47	54	64	60	64
	Bottom	37	53	64	59	59

The data shows that Composite B which contains the donor EDMAB exhibits significantly greater bottom polymerization when post-cured for 5 or 20 more minutes at 25°C or 20 minutes at 37°C, compared to Composite A without EDMAB. The electron donor EDMAB provides enhanced cure speeds for thick sections of epoxy/polyol/acrylate composites.

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Example 12

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Dental restorative pastes were prepared from each of the five light curable epoxy/polyol resin formulations shown in Table 8. The filler for each was prepared from a blend of 95 wt% finely milled P-10™ quartz filler (~3 micron APS) and 5 wt% fumed silica OX-50 (Degussa Inc.). The two silica based filler

were blended in a 1000 ml beaker, then slurred overnight in a 3-3.5 pH hydrolyzed aqueous solution of 5% (based on filler weight) 3-glycidoxypropyltrimethoxy silane. The slurry cake was dried at 60°C for 12 hours, crushed and screened through a 74 micron nylon screen. After a final drying of 80°C for two hours the filler was hand spatulated into the resins in 8-10 gram batch sizes to either 82.0% or 82.5% filler weight loading.

The resulting pastes were then tested for compressive strength and diametral tensile strength after irradiation with two Visilux-2 dental curing lights for 80 seconds in 1/8" ID Lexan tubing and after a post cure of 24 hours in 37°C distilled water.

Table 9 LIGHT CURED EPOXY FORMULATIONS WITH DPISbF6 IN EPOXY/POLYOL RESIN								
WEIGHT OF COMPONENTS PER 100 GRAM						Compressive	Diametral	Wt. %
CPQ	DPISbF6	EDMAB	EPON 828	UVR-6105	pTHF (250)	Strength (MPa)	Tensile (MPa)	Silane treated Quartz
(grams)	(grams)	(grams)	(grams)	(grams)	(grams)	24 hr.	24 hr.	
						(n=5)*	(n=5)*	
0.75	0.50	0.00	30.00	60.00	10.00	247 (10)	69.5 (1.8)	82.0
0.25	0.50	0.00	60.0	30.00	10.00	233 (11)	60.7 (8.6)	82.0
0.75	2.00	0.75	53.33	26.67	20.00	259 (7)	70.2 (5.0)	82.0
0.50	1.00	0.19	42.50	42.50	15.00	262 (6)	75.6 (1.7)	82.0
0.50	1.00	0.19	42.50	42.50	15.00	312 (7)	82.7 (9.4)	82.5
					*Numbers in () are standard deviations of 5 test values (n).			

Example 13 (Preparative Example)

A bifunctional aliphatic epoxy/acrylate material was prepared according to the following procedure:

UVR 6105 Cycloaliphatic diepoxide (109.6 grams, 0.44 moles) was transferred to 250 ml three-necked resin flask which was fitted with a condenser,

an air driven stir rod with a Teflon stir blade and an additional funnel. The system was kept dry with a calcium sulfate drying tube. The resin reactor was partially immersed in an oil bath heated to about 100C and the diepoxide allowed to equilibrate for about 30 minutes. Triphenyl antimony (0.3 grams) was transferred to the diepoxide and allowed to dissolve for about 15 minutes. Methacrylic acid (8.6 grams, 0.11 moles) was weighed into the addition funnel and then slowly added to the heated diepoxide slowly over about 3 hours. The mixture was allowed to react for a total of 24 hours yielding a liquid somewhat higher in viscosity than the starting materials. The bifunctional epoxy/acrylate material therefore had about one fourth (1/4) of the epoxy functionalities reacted with the unsaturated acid. The resulting resin is referred to hereinbelow as "UVR 1/4."

Example 14

This example describes the preparation of twenty-one epoxy/methacrylate resin-based composite materials containing varying amounts of UVR 1/4 (described in example 13). UVR6105 (cycloaliphatic diepoxide), pTHF250 (aliphatic diol), HPMA (3-hydroxypropyl methacrylate), DPISbF₆ (an iodonium salt), CPQ (camphorquinone - an alpha-diketone) and EDMAB (ethyl-p-dimethyl aminobenzoate - an amine electron donor).

Twenty-one resin compositions were prepared as follows shown in Table 10. Each composition was prepared by combining the ingredients at room temperature and stirring until homogeneous.

Twenty-one composite materials were further prepared by combining 3.0 grams of the quartz filler OX-50 with 6.0 grams of Compositions in Table 10 respectively. Samples were spatulated until a thick homogeneous paste was obtained.

Samples were evaluated for photopolymerization by determining the BarCol A hardness of 2mm thick sample according to the following procedure. A 2mm thick Teflon block which had a cylindrical hole measuring about 6mm diameter that extended through the thickness of the block was placed on a film of transparent polyethylene terphthalate (PET) such that one end of the open

cylindrical hole of the die was covered by the PET film. The Teflon die was filled with the sample and another film of PET placed on top of the die covering paste sample. Hand pressure was applied to the PET film to provide an approximately 2mm thick sample. Samples were irradiated with the Visilux 2 light source for 60
5 seconds by placing the light wand directly on the PET film which covered the sample at the top of the die. Three sets of samples were prepared in triplicate and stored for 10 minutes and 24 hours at 25C and 24 hours at 37°C respectively. After storage, the PET films were removed and the hardness of the top and bottom of the die was measured using a Barber-Coleman Impressor (a hand-held portable
10 hardness tester; Model GYZJ 934-1; from Barber Coleman Company Industrial Instruments Division, Lovas Park, IN) equipped with an indenter. For each sample tested, three readings were taken at the top and bottom of each sample. The readings were averaged for each composition and storage condition. A hardness value of zero indicated limited or no polymerization. Bottom hardness values
15 significantly less than those of the top indicate limited depth of cure. Results are summarized in Table 10 below.

Table 10												
Composition of Samples												
Sample #	UVR 1/4	UVR6105	pTHF250	HPMA	CPQ	DPISbF ₆	EDMAB	Barcol Hardness Testing				
								10 min RT	24 hr RT	24 hr 37C		
								top/bottom	top/bottom	top/bottom		
a	1.82	7.58	0.50	0.10	0.05	0.125	0.01	33/0	66/56	44/33		
b	7.58	1.62	0.50	0.10	0.05	0.125	0.01	0/0	36/24	52/46		
c	1.54	6.38	1.74	0.34	0.05	0.125	0.01	53/52	59/50	37/55		
d	6.38	1.54	1.74	0.34	0.05	0.125	0.01	57/53	57/54	57/59		
e	1.82	7.58	0.33	0.26	0.05	0.125	0.01	62/57	40/57	63/62		
f	7.58	1.82	0.33	0.26	0.05	0.125	0.01	0/0	47/19	56/56		
g	1.52	6.38	1.15	0.93	0.05	0.125	0.01	48/32	54/48	57/57		
h	6.38	1.53	1.15	0.93	0.05	0.125	0.01	27/26	51/32	58/56		
i	4.29	4.30	0.99	0.47	0.05	0.125	0.01	17/0	55/51	52/58		
j	4.29	4.30	0.93	0.47	0.05	0.125	0.01	38/19	53/46	59/61		
k	4.29	4.30	0.93	0.47	0.05	0.125	0.01	20/0	51/43	58/57		
l	4.29	4.30	0.93	0.47	0.05	0.125	0.01	16/0	52/50	59/58		
m	0.00	8.80	0.93	0.47	0.05	0.125	0.01	55/45	53/60	63/61		

Table 10												
Sample #	Composition of Samples							Barcol Hardness Testing				
	UVR 1/4	UVR6105	pTHF250	HPMA	CPQ	DPISbF ₆	EDMAB	10 min RT top/bottom	24 hr RT top/bottom	24 hr 37C top/bottom		
n	6.60	0.00	0.93	0.47	0.05	0.125	0.01	0/0	43/44	55/57		
o	5.00	5.00	0.00	0.00	0.05	0.125	0.01	0/0	26/17	51/49		
p	3.77	3.77	1.64	0.82	0.05	0.125	0.01	52/30	54/53	59/59		
q	4.30	4.90	1.40	0.00	0.05	0.125	0.01	55/50	52/56	57/57		
r	4.30	4.30	0.70	0.70	0.05	0.125	0.01	0/0	41/43	55/53		
s	4.30	4.30	0.83	0.47	0.05	0.125	0.01	18/0	44/95	54/54		
t	4.30	4.90	0.99	0.47	0.05	0.125	0.01	34/28	39/39	57/54		
u	0.00	8.00	2.00	0.00	0.05	0.125	0.01	63/54	61/62	65/63		

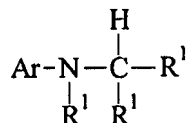
This example demonstrates that compositions containing bifunctional epoxy/acrylate materials and/or difunctional epoxy materials, and optionally containing hydroxy functional acrylates, together with polyols, provide resins that exhibit desirable cure properties. These compositions exhibit either
5 good initial cure properties or demonstrate a "living" cure system by hardening over time after initial exposure.

The above specification, examples and data provide a complete description of the manufacture and use of the composition of the invention. The
10 United States patents referred to in the foregoing specification are incorporated into the specification by reference. Since many embodiments of the invention can be made without departing from the spirit and scope of the invention, the invention resides in the claims hereinafter appended.

WE CLAIM:

1. A photopolymerizable composition comprising:
- (a) an epoxy resin;
 - (b) a hydroxyl-containing material; and
 - (c) a photoinitiator system comprising:
 - (i) an iodonium salt;
 - (ii) a visible light sensitizer; and
 - (iii) an electron donor compound, wherein the photoinitiator system has
- a photoinduced potential greater than or equal to that of 3-dimethylamino benzoic acid in a standard solution of 2.9×10^{-5} moles/g diphenyl iodonium hexafluoroantimonate and 1.5×10^{-5} moles/g camphorquinone in 2-butanone.

2. The composition of claim 1 wherein the donor compound is described by the following structural formula:



- wherein R^1 are independently H, C_{1-18} alkyl that is optionally substituted by one or more halogen, -CN, -OH, -SH, C_{1-18} alkoxy, C_{1-18} alkylthio, C_{3-18} cycloalkyl, aryl, COOH , COOC_{1-18} alkyl, $(\text{C}_{1-18} \text{ alkyl})_{0-1}-\text{CO}-\text{C}_{1-18}$ alkyl, SO_3H , CN or halogen groups, or aryl that is optionally substituted by one or more electron withdrawing groups where R^2 is H, C_{1-18} alkyl that is optionally substituted by one or more halogen, -CN, -OH, -SH, C_{1-18} alkoxy, C_{1-18} alkylthio, C_{3-18} cycloalkyl, aryl, COOH , COOC_{1-18} alkyl, $(\text{C}_{1-18} \text{ alkyl})_{0-1}-\text{CO}-\text{C}_{1-18}$ alkyl, SO_3H , CN or halogen groups, or aryl that is optionally substituted by one or more electron withdrawing groups, or the R^1 groups together may form a ring; and Ar is aryl that is substituted by one or more electron withdrawing groups.

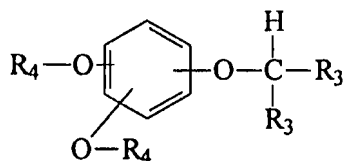
3. The composition of claim 2 wherein the aryl group is substituted by one or more carboxylic acid, carboxylic acid ester, ketone, aldehyde, sulfonic acid, sulfonate, or nitrile groups.

5 4. The composition of claim 2 wherein the aryl group is substituted by one or more moieties selected from the group consisting of -COOH, -COOC₁₋₁₈ alkyl, -SO₃R², -CN, -CO-C₁₋₁₈ alkyl and -C(O)H groups, where R² is H, C₁₋₁₈ alkyl that is optionally substituted by one or more halogen, -CN, -OH, -SH, C₁₋₁₈ alkoxy, C₁₋₁₈ alkylthio, C₃₋₁₈ cycloalkyl, aryl, COOH, COOC₁₋₁₈ alkyl, (C₁₋₁₈ alkyl)₀₋₁-CO-C₁₋₁₈ alkyl, SO₃H, CN or halogen groups, or aryl that is optionally substituted by one or more electron withdrawing groups.

15 5. The composition of claim 1 wherein the donor compound is selected from the group consisting of 4-dimethylaminobenzoic acid, ethyl 4-dimethylaminobenzoate, 3-dimethylaminobenzoic acid, 4-dimethylaminobenzoin, 4-dimethylaminobenzaldehyde, 4-dimethylaminobenzonitrile and 1,2,4-trimethoxybenzene.

20 6. The composition of claim 1 wherein the donor compound is an alkyl, aryl polyether.

7. The composition of claim 1 wherein the donor compound is an alkyl, aryl polyether having the structural formula:



25 wherein n = 1-3 each R₃ is independently H or C₁₋₁₈ alkyl that is optionally substituted by one or more halogen, -CN, -OH, -SH, C₁₋₁₈ alkoxy, C₁₋₁₈ alkylthio, C₃₋₁₈ cycloalkyl, aryl, substituted aryl, -COOH, -COOC₁₋₁₈ alkyl, -(C₁₋₁₈ alkyl)₀₋₁-COH, -(C₁₋₁₈ alkyl)₀₋₁-CO-C₁₋₁₈ alkyl, -CO-C₁₋₁₈ alkyl, -C(O)H or -C₂₋₁₈ alkenyl

groups, or the R^3 groups together may form a ring and each R_4 can be C_{1-18} alkyl that is optionally substituted by one or more halogen, -CN, -OH, -SH, C_{1-18} alkoxy, C_{1-18} alkylthio, C_{3-18} cycloalkyl, aryl, substituted aryl, -COOH, -COOC $_{1-18}$ alkyl, -
(C_{1-18} alkyl) $_{0-1}$ -COH, -(C_{1-18} alkyl) $_{0-1}$ -CO- C_{1-18} alkyl, -CO- C_{1-18} alkyl, -C(O)H or - C_{2-18} alkenyl groups.

8. The composition of claim 1 wherein the iodonium salt is an aryl iodonium salt.

9. The composition of claim 1 wherein the iodonium salt comprises diphenyliodonium chloride, diphenyl iodonium hexafluorophosphate, diphenyl iodonium hexafluoroantimonate, diphenyl iodonium tetrafluoroborate, or a mixture thereof.

10. The composition of claim 1 wherein the sensitizing compound comprises a ketone.

11. The composition of claim 1 wherein the sensitizing compound comprises an aliphadiketone.

12. The composition of claim 1 wherein the sensitizing compound comprises a ketocoumarin, aminoarylketone, or a para-substituted aminostyrylketone compound.

13. The composition of claim 1 wherein the sensitizing compound comprises camphorquinone.

14. The composition of claim 1 wherein the composition cures to a tack-free gel within 60 seconds after exposure to visible light.

15. The composition of claim 1 wherein the epoxy resin comprises a cycloaliphatic epoxide or diepoxide.

16. The composition of claim 1 wherein the epoxy resin comprises a bisphenol-A diepoxide.

17. The composition of claim 1 wherein the epoxy resin contains ethylenic unsaturation.

18. The composition of claim 1 further comprising an ethylenically unsaturated compound.

19. The composition of claim 16 wherein the ethylenically unsaturated compound is an ester of acrylic acid or methacrylic acid.

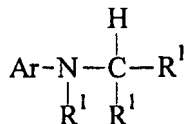
20. The composition of claim 16 wherein the ethylenically unsaturated compound comprises methyl acrylate, methyl methacrylate, ethyl acrylate, isopropyl methacrylate, n-hexyl acrylate, stearyl acrylate, allyl acrylate, glycerol diacrylate, glycerol triacrylate, ethyleneglycol diacrylate, diethyleneglycol diacrylate, triethyleneglycol dimethacrylate, 1,3-propanediol diacrylate, 1,3-propanediol dimethacrylate, trimethylolpropane triacrylate, 1,2,4-butanetriol trimethacrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, sorbitol hexacrylate or a mixture thereof.

21. A photopolymerizable composition comprising:

- (a) an epoxy resin;
- (b) a hydroxyl-containing material; and
- (c) a photoinitiator system comprising:

(i) a diaryliodonium hexafluoroantimonate or diaryliodonium hexafluorophosphate;

- (ii) camphorquinone and
 (iii) an electron donor described by the following structural formula:

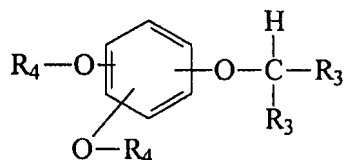


- 5 wherein R¹ are independently H, C₁₋₁₈ alkyl that is optionally substituted by one or more halogen, -CN, -OH, -SH, C₁₋₁₈ alkoxy, C₁₋₁₈ alkylthio, C₃₋₁₈ cycloalkyl, aryl, COOH, COOC₁₋₁₈ alkyl, (C₁₋₁₈ alkyl)₀₋₁-CO-C₁₋₁₈ alkyl, SO₃H, CN or halogen groups, or aryl that is optionally substituted by one or more electron withdrawing groups where R² is H, C₁₋₁₈ alkyl that is optionally substituted by one or more
 10 halogen, -CN, -OH, -SH, C₁₋₁₈ alkoxy, C₁₋₁₈ alkylthio, C₃₋₁₈ cycloalkyl, aryl, COOH, COOC₁₋₁₈ alkyl, (C₁₋₁₈ alkyl)₀₋₁-CO-C₁₋₁₈ alkyl, SO₃H, CN or halogen groups, or aryl that is optionally substituted by one or more electron withdrawing groups, or the R¹ groups together may form a ring; and Ar is aryl that is substituted by one or more electron withdrawing groups.

15

22. A photopolymerizable composition comprising:

- (a) an epoxy resin;
 (b) a hydroxyl-containing material; and
 (c) a photoinitiator system comprising:
 20 (i) a diaryliodonium hexafluoroantimonate or diaryliodonium hexafluorophosphate;
 (ii) camphorquinone and
 (iii) an electron donor described by the following structural formula:



25

wherein $n = 1-3$ each R_3 is independently H or C_{1-18} alkyl that is optionally substituted by one or more halogen, -CN, -OH, -SH, C_{1-18} alkoxy, C_{1-18} alkylthio, C_{3-18} cycloalkyl, aryl, substituted aryl, -COOH, -COOC $_{1-18}$ alkyl, -(C_{1-18} alkyl) $_{0-1}$ -COH, -(C_{1-18} alkyl) $_{0-1}$ -CO-C $_{1-18}$ alkyl, -CO-C $_{1-18}$ alkyl, -C(O)H or -C $_{2-18}$ alkenyl groups, or the R^3 groups together may form a ring and each R_4 can be C_{1-18} alkyl that is optionally substituted by one or more halogen, -CN, -OH, -SH, C_{1-18} alkoxy, C_{1-18} alkylthio, C_{3-18} cycloalkyl, aryl, substituted aryl, -COOH, -COOC $_{1-18}$ alkyl, -(C_{1-18} alkyl) $_{0-1}$ -COH, -(C_{1-18} alkyl) $_{0-1}$ -CO-C $_{1-18}$ alkyl, -CO-C $_{1-18}$ alkyl, -C(O)H or -C $_{2-18}$ alkenyl groups.

10

23. A method for photopolymerization comprising the step of irradiating a photopolymerizable composition with light having a wavelength between about 400 and 1000 nanometers until said composition gels or hardens, said composition comprising:

15

- (a) an epoxy resin;
- (b) a hydroxyl-containing material; and
- (c) a photoinitiator system, said photoinitiator system comprising:
 - (i) an iodonium salt;
 - (ii) a visible light sensitizer; and
 - (iii) an electron donor compound, wherein the photoinitiator

20

system has a photoinduced potential of at least about 100mV relative to a standard solution of 2.9×10^{-5} moles per gram diphenyliodonium hexafluoroantimonate and 1.5×10^{-5} moles per gram camphorquinone in 2-butanone.

25

24. The method of claim 23 wherein the composition additionally comprises an ethylenically unsaturated compound.

30

25. A photopolymerizable dental composition comprising:

- (a) an epoxy resin;
- (b) a hydroxyl-containing material; and

- (c) a photoinitiator system comprising:
- (i) an iodonium salt;
 - (ii) a visible light sensitizer; and
 - (iii) an electron donor compound, wherein the photoinitiator
- 5 system has a photoinduced potential of at least about 100mV relative to a standard solution of 2.9×10^{-5} moles/g diphenyl iodonium hexafluoroantimonate and 1.5×10^{-5} moles/g camphorquinone in 2-butanone.

10 26. A composition of claim 25, wherein said composition is a dental adhesive.

27. A composition of claim 25, wherein said composition is a dental composite material.

15 28. A composition of claim 25, wherein said composition is a dental sealant.

20 29. A composition of claim 25, wherein said composition is an orthodontic adhesive.

30. A composition of claim 1, wherein said composition is a graphic arts imaging composition.

25 31. A composition of claim 1, wherein said composition is selected from the group consisting of photoresists, solder masks, electronic conformal coatings, coated abrasives and magnetic media compositions.

INTERNATIONAL SEARCH REPORT

In tional Application No

PCT/US 98/04458

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 G03F7/038 G03F7/029 A61K6/087 A61K6/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G03F C08G A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 13538 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 9 May 1996 cited in the application see page 31, line 3 - line 20 ---	1-31
A	EP 0 290 133 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 9 November 1988 cited in the application * page 7, run no. 21, 25 and 31 * -----	1-31

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search

12 June 1998

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/04458

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9613538 A	09-05-1996	AU 3971895 A EP 0789721 A	23-05-1996 20-08-1997
EP 0290133 A	09-11-1988	CA 1323949 A JP 2744789 B JP 63273602 A US 5545676 A	02-11-1993 28-04-1998 10-11-1988 13-08-1996

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